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THE MANUFACTURE OF SULPHURIC ACID AND ALKALI

VOLUME I.—PART I.

THE MANUFACTURE
SULPHURIC ACID AND ALKALI

WITH THE

COLLATERAL BRANCHES

A THEORETICAL AND PRACTICAL TREATISE

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PART I

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PREFACE TO FOURTH EDITION

THE last edition of this volume appeared in the year 1903. It is hardly necessary to say that since then the chemical industries treated therein have made vast strides forward, not merely in respect of quantitative extension, but also in the methods of manufacture. It seems, therefore, full time to register this progress, which I have been enabled to do by personal observation as well as by a great number of communications made to me, apart from the vast amount of material contained in the technical publications and in the patent specifications during this time.

I have done my best to embody this fresh matter with that contained in the former editions, and I trust the readers of this Treatise will give me credit for my endeavours to keep it up to its standard of usefulness, and that they will excuse the errors and omissions inevitable when dealing with such a vast subject.

The considerable amount of new matter published in this field during the printing of this volume has been embodied in the Addenda, so as to bring up the subject to the present date.

G. LUNGE.

ZURICH, *February* 1913.

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FIRST BOOK

SULPHURIC ACID

INTRODUCTION

FORMERLY the term "alkali manufacture" nearly always comprised a cycle of operations, beginning with the manufacture of sulphuric acid and proceeding to that of sulphate of soda (salt-cake), hydrochloric acid, soda-ash (with caustic soda, soda-crystals, etc.), and bleaching-powder. This cycle is not completed in all factories, but frequently (at the present day even more so than formerly) the operation stops at sulphuric acid or sulphate of soda; but we may embrace all this under the general term of "Sulphuric Acid and Alkali Manufacture."

In this wider meaning the products of alkali-making are necessary materials for many metallurgical processes, for the manufacture of artificial manures, soap, fatty and mineral oils, glass, paper, many inorganic and organic colouring-matters (especially nearly all coal-tar dyes), and even of many articles of food,—that is to say, for nearly all branches of manufacturing chemistry. In fact, among all branches of chemical industry the cycle of technical operations connected with alkali-making is pre-eminent, not merely from the magnitude of the works and the absolute bulk of the raw material used and the quantity produced, but also from the fact that most other chemical products require one or more branches of alkali-making as the conditions of their own existence. It can be truly said that the manufacture of acids and alkali is the foundation upon which the whole chemical industry of our times is built up, and that such industry cannot be much developed in any country not possessing a flourishing alkali trade, or not being at least specially well situated for buying the produce of the latter. It is thus evident how great is the importance of the alkali trade in its wider meaning to the civilisation of mankind, though we should certainly be going too far if we measured, as some have done, the civilisation of a country by the development of this special industry.

Formerly the whole cycle of processes here described was intimately connected with the great invention of Leblanc, now a century and a quarter old. Thirty years ago, although the ammonia-soda process had then already more than proved its right to be considered a full success, it had not yet shaken in any tangible degree the supremacy of the Leblanc process, at least not in Great Britain. In the latter process the different branches of "alkali-making" mentioned above are connected in such a manner that only under special local conditions can one or more of the principal substances be omitted. Formerly this was the case even less than now, as the competition of ammonia-soda ash and electrolytical methods have completely altered some of the conditions of trade, making it unremunerative in many cases to convert the sulphate of soda into the carbonate. Many works now stop at the manufacture of sulphuric acid; others go as far as sulphate of soda, together with chlorine products; but many proceed still further, going on to the manufacture of soda in its various branches.

The manufacture of *sulphuric acid* is in reality a very large industry, quite apart from its connection with the Leblanc process. Enormous quantities of it are required for the manufacture of artificial manures (fertilisers), and therefore every large manure factory makes its own sulphuric acid. This is done also by the largest sulphate-of-ammonia works, petroleum refiners, coal-tar dye manufacturers, and in a few other cases. Some works in England, and many on the Continent, make sulphuric acid to a great extent, or even entirely, not for their own use, but for sale. Since this acid is no longer sent out in any considerable quantity in glass carboys, but in iron tank-waggons, it can be carried to considerable distances at moderate cost.

As sulphuric acid is mostly made from pyrites, its manufacture is intimately connected with the recovery of *copper* from the cinders, in which process ferric oxide, silver and other by-products are obtained.

A very large (formerly even the largest) quantity of sulphuric acid is used up at the works themselves for the manufacture of *sulphate of soda* (*salt-cake*) and *sulphate of potash*, in which *hydrochloric acid* is a necessary by-product. Sometimes salt-cake is obtained without previously manufacturing sulphuric acid, as a by-product of other manufactures or by the 'direct process" of Hargreaves and Robinson. Salt-cake is used on a very large scale for the manufacture of glass; and perhaps even more of it still enters into the *Leblanc process for manufacturing soda*. This article is mostly the final product, either in the calcined or crystallised or caustic state, and the series of operations is thus brought to a close in this direction.

Hydrochloric acid (*muriatic acid*) is, of course, sold as such to some extent, but in nothing like such large quantities as sulphuric acid, as its carriage is impossible in metallic vessels, and therefore more expensive and troublesome. Most of it is at once, sometimes even without condensation to liquid acid, converted into *chlorine*, which, being a gas, is immediately worked up into bleaching-powder or chlorate of potash, or occasionally into other products; a comparatively small quantity of it is sold in the state of liquid chlorine. The time when the hydrochloric acid was condensed merely to satisfy the exigencies of laws made for protecting the health and vegetation of a neighbourhood, and was then run to waste into the nearest watercourse, is long ago past, since the process of decomposing salt by sulphuric acid is only profitable if the hydrochloric acid is fully utilised; this acid has thus in many cases risen from the rank of a by-product to that of the best-paying principal product.

Since the conditions of the Leblanc process have been further changed by the solution of the problem of the *recovery of sulphur* from the alkali waste, it has been made into a real cycle, into which common salt and coal enter at one end, alkali and chlorine issuing at the other, whilst sulphur and possibly even lime are made to do service over and over again. This, however, appears most clearly in Vols. II. and III. of this treatise; to which we also refer for such general observations as the ammonia process of soda manufacture calls for.

The last, and a very fundamental change of the conditions of what is comprised by the term "alkali manufacture" has been effected by the development of the *electrolytic manufacturing process*, which must be relegated to a special volume, except those processes which deal with the production of nitrogen oxides and oxide from free nitrogen or ammonia; these are dealt with in their proper place in this present volume.

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CHAPTER IV

THE PRODUCTION OF SULPHUR DIOXIDE

A. FROM BRIMSTONE

ALREADY in the historical part attention has been drawn to the point that important progress was made in the manufacture of sulphuric acid when the periodical combustion of sulphur within the acid-chambers was replaced by continuous work in special apparatus attached to the chambers. This led to making the sulphur-burners altogether independent of the chambers, and conveying the gas generated in the former by a flue into the latter.

Whilst in the old periodical style of working only the oxygen actually present in the chamber could come into play, and therefore after every combustion the chamber had to be supplied with fresh air by opening the door and a special valve, of course at the expense of much inconvenience and loss of gas, in the continuous method of work the necessary air constantly enters the burner by suitable openings at the same rate as the products of combustion are aspirated into the chamber by the draught prevailing throughout the apparatus. The continuity of work must be further aided by employing a combination of several burners, so that there is always burning sulphur present. Or else burners are employed to which the brimstone is continuously supplied, in order to avoid the drawback of irregular supply of air and gas occurring even with the combination of several ordinary burners.

The plainest sulphur-burners, such as were formerly the most usual in England, are represented in Figs. 58 to 60. The burner consists of a brick chamber covered by an arch, the bottom being formed by a cast-iron plate, *a*, separately shown in Fig. 60. This plate at the two long sides and one of the ends has a somewhat slanting-up flange of 3 in. height—in front, however, only 1 in., so as to get out the ashes more easily. The plate does not go right through the burner, but leaves the last third of it free; in this part of the chamber the sulphur vapour, which is always formed, can mix with the excess of air and be burned. Rarely, however, is this completely attained, and there is generally some unburned sulphur

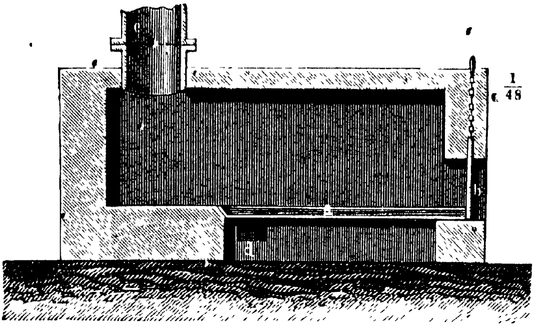

Fig. 58.

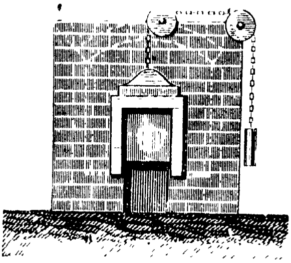

Fig. 59.

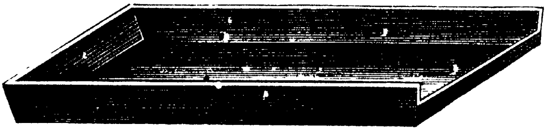

Fig. 60.

carried away. This not only causes a loss, but also easily leads to the chamber-acid getting muddy and being covered with a thin film of sublimed sulphur, thus preventing the contact between the bottom acid and the gas, which is most necessary for the chamber process. The burner is further provided with an iron door, *b*, sliding in a frame and adjustable by a chain and balance-weight; also with a pipe, *c*, for taking away the gas. An air-channel, *d*, below the plate is in connection with a small chimney, or sometimes only with the open air, in order to cool the metal plate to some extent and prevent the sublimation of sulphur. There are always several furnaces of this kind combined together; each of them, with plates of 8 ft. × 4 ft., can burn 5 cwt. of brimstone in twenty-four hours, which is put in in six portions, one every four hours; if four furnaces are combined, one of them is charged every hour. Sometimes, however, much larger and more frequent charges are made (see below [1]). Frequently in these burners, usually at the same time, the nitric acid is liberated by placing cast-iron pots, provided with three feet and containing a mixture of nitre and sulphuric acid, amidst the burning sulphur by means of large tongs.

For a start the plates are heated by a small fire of wood shavings, the door being left open, not till the iron becomes red-hot, but only till the first charge of sulphur ignites of its own accord or can be easily lighted by a red-hot iron; the further charges always find the burner sufficiently warm. A special fire-grate below the plate, to be used only at the start, is sometimes provided, but is quite unnecessary. The admission of air is regulated by opening the door, *b*, more or less widely; and its position is fixed by putting a wedge underneath it, or by hooking the balance-chain to a nail driven into the brickwork outside. At the commencement, when the chambers are filled with air, the damper in the draught-tube is only opened gradually, to drive away the air more thoroughly.

The style of working is generally rather rough; we must consider that such burners are nowadays hardly ever found in large works, where more supervision can be used. Before the attendant pulls up the door, he convinces himself regarding the state of the chambers, so as to judge how much nitre he is to "pot" along with the brimstone. Sometimes (in former times regularly) the nitre is merely measured by guesswork. First the brimstone is thrown in; the door is immediately let down; then a sufficient quantity of chamber-acid is poured into the nitre-pots, always by guesswork; the door is opened again, and the pots are placed in the brimstone, now already on fire, by means of an iron fork made for the purpose. The heat produced by the progress of the combustion drives off the nitric acid, and this enters the chambers together with the sulphur dioxide.

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[1] Davis (*Chemical Engineering*, ii. p. 123) states that up to 2 lb. of brimstone can be burned per square foot per hour. This is more than the maximum I have ever found in practice. It is best not to reckon upon much more than 1 lb. per square foot per hour.

When the time is up, the door is raised again, and the ashes are raked out; first, however, the nitre-pots are lifted out and emptied of their liquid contents. Then a new charge is made as above, and so forth. In all other sulphur-burners, excepting the continuous ones, the work is carried on in the same manner; only the introduction of the nitre sometimes takes place in a less rough way, or nitric acid is run directly into the chambers.

It is a sign that the burner is working well if the brimstone burns with a pure blue flame; as soon as the flame takes a brown tinge, it indicates that much sulphur is subliming, and care must then be taken to cool the plate by the flue underneath.

A somewhat more perfect apparatus is shown in Fig. 61. A is the foundation, B the chamber for burning the sulphur, C the gaspipe. The foundation carries a cast-iron plate which covers the whole furnace-bottom and is inclined a little forward. The combustion-chambers are at the sides bounded by brick walls, but in front, at the back, and at the top by cast-iron plates; in front also are the charging-doors, *b b*, and small openings, *a a*, provided with slides for regulating the access of air. The furnace-bottom is divided by 3- or 4-in. iron bars into three compartments, corresponding to the doors and draught-holes, which are served by turns. Inside the pots are visible, into which the mixture of nitre and sulphuric acid is charged. The details of construction are often very different from those shown in the diagram; there are burners with more or fewer working compartments, with different regulation of air, with rails over the bottom plates for pushing in a box instead of the nitre-pots, etc. The nitre-pots must receive a very small charge, otherwise the danger of boiling over is considerable, and the sodium sulphate getting into the sulphur is very troublesome. When nitric acid is used in the chambers, the nitre-pots are not required at all.

Sometimes the iron sides of the sulphur-burners are made double, and an air-channel is left in the space between. Thus, of course, the temperature of the burner can be regulated to a nicety by opening up a draught through the double iron wall when the burner gets too hot, and shutting up the draught when it gets too cold.

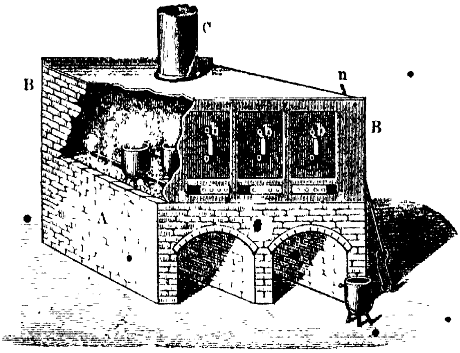


FIG. 61.

The diagrams Figs. 62 to 65 show a set of two burners free from most of the drawbacks mentioned. Fig. 65 is a sectional plan taken at two different levels; Fig 64 a longitudinal section; Fig. 62, half front elevation, half cross-section; Fig. 63, back elevation.

a is the cast-iron bottom plate for burning the sulphur; it is carried hollow on pillars; and the channels *b b* formed thereby underneath the plate communicate with the outer air by the opening *c*, so that the plate can be cooled from below. The channels, *d d*, left in the foundation a little further below, communicate with this system, and ultimately end outside *d'*. Owing to the difference of level and temperature, the air must always enter at *d'* and get out at *c*; its quantity can be easily regulated by partially closing *c*. The door *e* is hung in the usual way. The gas of the burner does not go straight to the

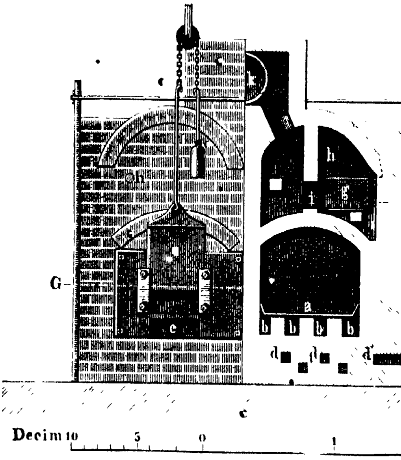


FIG. 62.

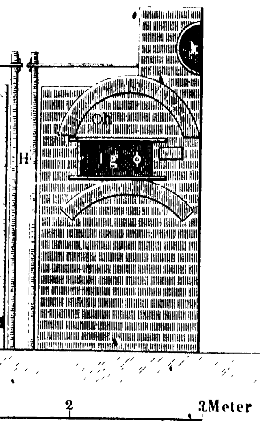


FIG. 63.

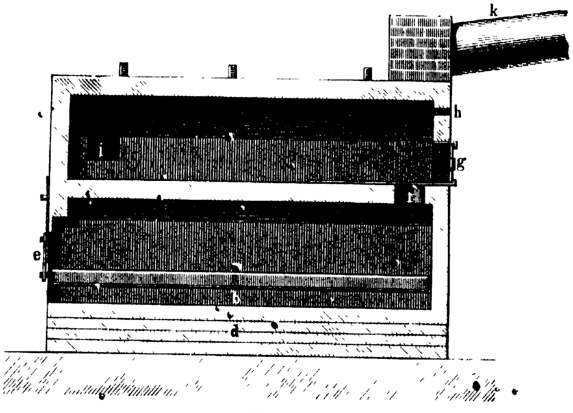


FIG. 64.

chamber, but first ascends through the opening *f* into a space separated from the burner proper by an arch. Just above the opening there is a grating, on which the nitre-pots are put, being introduced by the door *g*. There is here a small hole, *h*, lined with an iron tube, for admitting a little more air to the upper compartment and burning any sublimed sulphur. The gas first returns to the front, then back again through the hole *i* and the second half of the upper compartment, and at last escapes through the cast-iron pipe *k*, common to two burners, whose upper stories are accordingly not built alike, but are symmetrical.

This burner (known to myself from actual use) admits of very good regulation ; any subliming sulphur on its long course through the upper story is either deposited as such or burnt, and cannot get into the chambers. The boiling-over of the nitre-pots can here be rendered harmless by simple contrivances. This burner is in some points analogous to that of Harrison Blair (see p. 400), but it is much simpler and adapted for a smaller scale of work. As a rule the working-doors are closed within a very small fraction, and the admission of air to the upper story is regulated by more or less closing the hole *b*. Four such furnaces work together; every half-hour one of them is charged with ½ cwt. of brimstone.

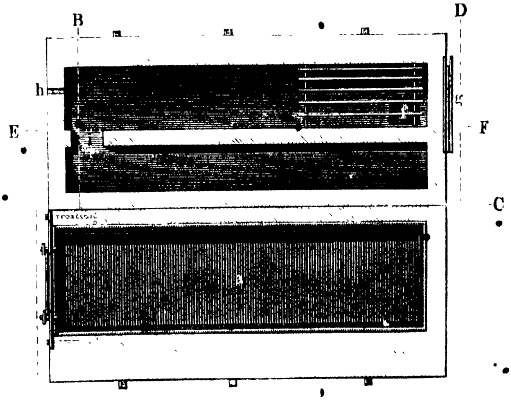


FIG. 65.

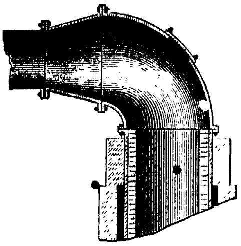
Fish (B. P. 7757 of 1891) makes the burner-bed incline to one side, so that the sulphur can be gradually moved towards that side, where the ashes are raked out.

In order to avoid the drawback common to all sulphur-burners, viz., the high temperature which causes a sublimation of sulphur (which some have tried to avoid by wetting the brimstone with water), and even to turn it to some use, the cover of the burner is occasionally employed for drying wet materials; it has sometimes been made in the shape of a pan for heating water or for concentrating acid, which is the most rational plan.

A large brimstone-burner, covered in with evaporating-pans, is shown in Figs. 66 to 68. Fig. 66 is a sectional elevation on the lines E F G H of Fig. 67; Fig. 67 is a plan on lines A B C D of Fig. 66; Fig. 68 a front view. These diagrams, representing a furnace at work in America, have been kindly supplied by Dr Karl F. Stahl, of Johnstown (Pa.). Its bottom, roof, and sides are formed of cast-iron plates, 1 in. thick, with 6-in. flanges bolted together and caulked with rust-cement. A brick wall, 9 in. thick, is carried all round, leaving a hollow space of 2 in. from the plates; a few of the bricks near the top and bottom are put in loosely, which permits of air-cooling in very hot weather. The lead pans placed on the iron roof are 3′ 6″ × 10′ 10″ × 7″, the weight of the lead being from 8 to 12 lb. per super. foot. The furnace bottom consists of five plates, as seen in Fig. 66; on each of the three front plates (3′ 6″ × 12′) from 1000 to 1300 lb. of brimstone can be burnt in twenty-four hours.

An arrangement, made by Kuhlmann, for combining a steam-boiler with a sulphur-burner (1st edition of this work, pp. 139, 140), did not answer at all, and has been discontinued.

All the sulphur-burners hitherto described are built on the intermittent plan; and unless a number of them were working together, they would yield a very unequal current of gas. As the sulphur must, of course, be allowed to burn off as completely as possible, the furnace in the final stage, and especially just before being recharged, yields very little sulphur dioxide, whilst it is not possible to regulate the draught so that exactly so much less air is introduced as less sulphur is burnt. When at last the door is opened for a new charge, a very large quantity of air rushes into the burner and further on to the chambers, without any sulphur dioxide whatsoever. This irregularity, very prejudicial to the chamber process, is certainly to a great extent neutralised by the fact that always several furnaces



Scale $\frac{1}{71}$.

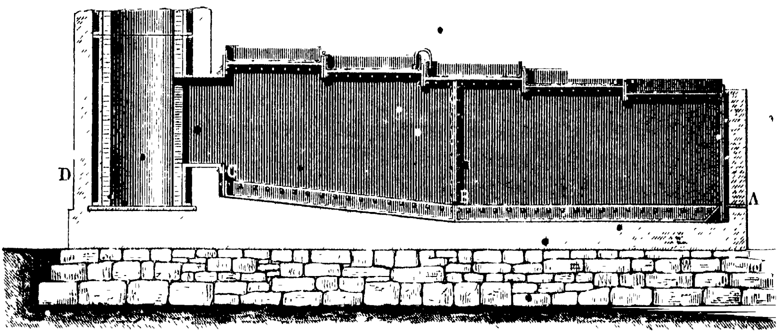


FIG. 66

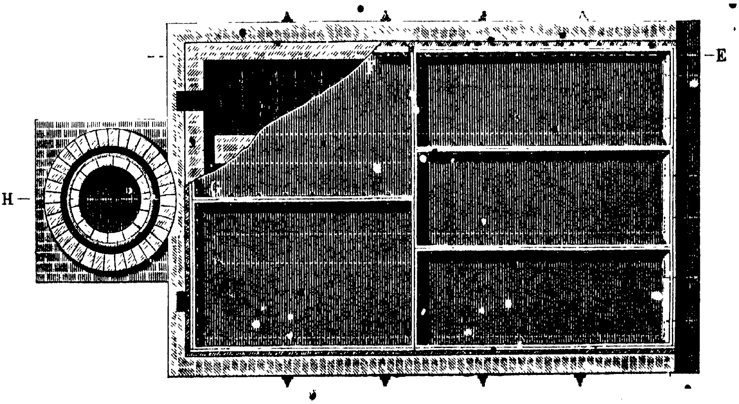


FIG. 67.

(three, four, five, or more) work together in such a way that they are charged in turns; for instance, with a four hours' shift and four furnaces one furnace is charged every hour, and thus gives out least gas when its neighbours are fully burning.

The just-mentioned irregularity is entirely avoided by the application of *continuous burners*, which save much labour, and, moreover, give a much better regulated current of gas than can be obtained with single burners.

Two such continuous burners have been constructed by Petrie; we refer for diagrams and descriptions to our 1st edition, pp. 141 and 142.

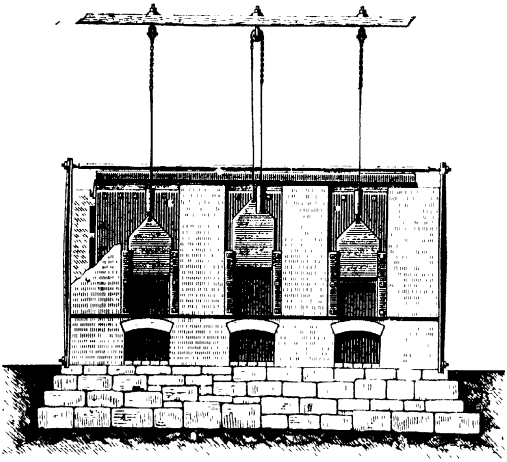


FIG. 68.

The object pursued by Petrie is attained in a more perfect way by the furnace of Harrison Blair, in which the volatilisation of the sulphur, which otherwise is a source of inconvenience, is utilised to make the burning continuous. The apparatus consists of three parts, one of which serves for partly burning the sulphur and entirely volatilising the unburnt portion; the second serves for completely burning the latter portion; the third for decomposing the nitre. Although the two former compartments are at a full red-heat during the process, no sublimation of sulphur practically takes place, and the process is as nearly continuous as possible, since the residue need only be withdrawn once in twenty-four hours. Fig. 69 shows a plan, Fig. 70 a sectional elevation, of this burner. A is the space corresponding to an ordinary burner-plate, which has rather high sides and a descent towards the door; but 2 ft. from the door it rises again a little, so that the residue raked to that part can burn out completely before it is removed by the door B, which

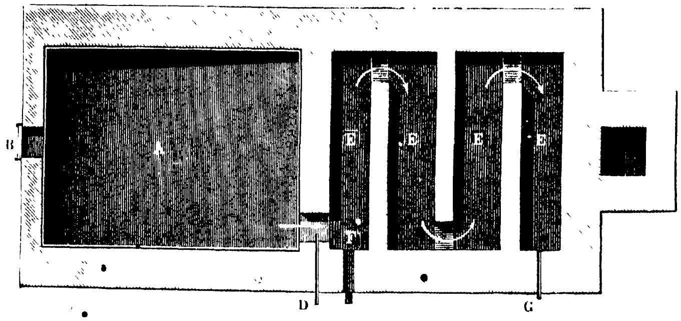


FIG. 69.

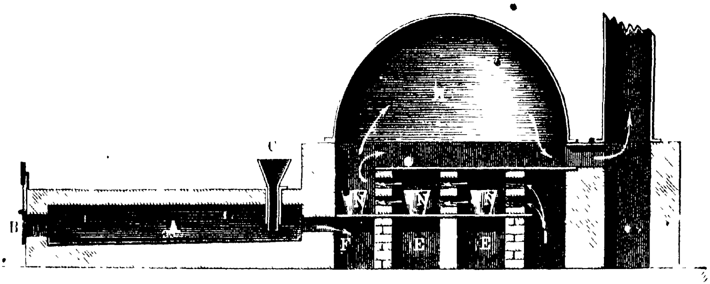


FIG. 70.

takes place once in twenty-four hours. When this has been done, the residue raked together from the other parts of the burner is brought to the same place and allowed to burn for twenty-four hours again. The bottom of the burner is not made of iron, but of closely-set bricks with well-grouted joints. This space A is 9 ft. long, 6 ft. wide, and [illegible] ft. high. The door B is an iron plate, loosely sliding in a frame, but a little slanting so that it closes almost air-tight, and is easily removed. It is perforated by a number of holes, which can be either partly c entirely closed by a slide. The brimstone is either put in onc every twenty-four hours through the working-door, or graduall through a funnel C. C is continued by a 7-in. cast-iron pipe t within 6 in. from the bottom of the chamber; it is surrounded b a wider pipe to protect it against being burnt too quickl The funnel and its continuation are always filled with brim stone; and this is continually replaced as it melts off at th bottom. The simpler method of charging once every twenty four hours through the door seems after all to have succeeded bes The admission of air through B is regulated so that only suff cient sulphur is burnt for keeping up the heat of the furnace most of it is simply evaporated. At the same time the regu lation of the access of air allows of spreading the proces evenly over the whole day. The walls of the furnace are mad 1½ brick thick, in order to retain the heat. The mixed gas an vapours enter through an opening of 9×9 in. (which be closed by a fire-clay damper D) into the combustion-spac proper, E E, 8×6 ft., divided by three partitions into fou compartments, communicating alternately in front and back b openings 9 in. square. Here at the same time fresh air enter by the opening F, which is provided with a damper of 3×8 i Now sufficient air is admitted for burning all the sulphur, whic can be recognised with certainty by the fact that on openin the plug G the entering air does not produce a new flame. Th roof of the combustion-space, E, is formed of fire-tiles, abov which a second story, the nitre-oven, is situated. There ar three rows of nitre-pots, N, separated by reticulated brickwork which also serves to support another roof of fire-tiles for cover ing the nitre-oven, altogether 18 in. high. The diagram show how the hot gas circulates round the nitre-pots. The pots ar renewed every six hours, so that every two hours another ro of pots has its turn. The hot gas, mixed with the nitre-ga first passes underneath the cast-iron dome, H, for a partia cooling, then through an iron pipe, 24 ft. high, into a smal cooling-chamber 18 ft. long, 5 ft. wide, and 1½ ft. high (whos bottom and top are covered with water), and then into the lead chambers. Sometimes steam is admitted into the combustion furnace, which is said to hasten the formation of sulphuric acid With a furnace of the dimensions stated, 26 tons of brimstone per week are said to have been burnt in a perfectly satisfactory way, corresponding to the work of 15 ordinary burners; by cutting off part of the air it was possible to reduce the sulphur burnt to 5 or 6 tons per week. For an equal chamber-space much more sulphur can be burnt than with ordinary burners without any damage to the process, owing to the even work and the avoiding of any excess of air. Indeed Blair's burner is much commended, and probably would have been more extensively employed, but that soon after its invention most large works (and only such can do with it) passed over from brimstone to pyrites.

At the present time, of course, nobody would think of such a way of cooling the gas as is shown here in the cast-iron dome H. We should employ its heat in a Glover tower, or previously for concentrating acid. We should also replace the potting arrangement shown in the diagram by the more perfect arrangements to be described later on in connection with pyrites-kilns; or we should leave it out altogether, and supply the chambers with liquid nitric acid through the Glover tower.

A modification of the principle of burning the subliming sulphur by introducing air behind the burner was patented by H. Glover (No. 3774 of 1879). He arranges behind the burner a chamber, loosely packed with bricks, in which the vaporised sulphur deposits before it can get into the lead-chambers. This brick chamber, when it is partially filled with sublimed sulphur, is burned out by admitting air into it. The heat is utilised for concentrating acid, and the gases are eventually passed into a Glover tower, where they do all the necessary denitrating work. This system is at work at a Philadelphia factory, and gives entire satisfaction, as observed by myself, no repairs having been required after the lapse of five years.

This arrangement is shown in Fig. 71. A is the usual burner-plate, B the feeding-apparatus (on the same principle as used in Blair's burner); the burner-gases, with the subliming sulphur, pass into the chamber C, where they meet air entering through the pipes F, either cold or previously heated by waste heat. The mixture further passes through chamber D, containing a network of fire-bricks like that used in a Siemens' recuperator; the mixture and combustion here become perfect,

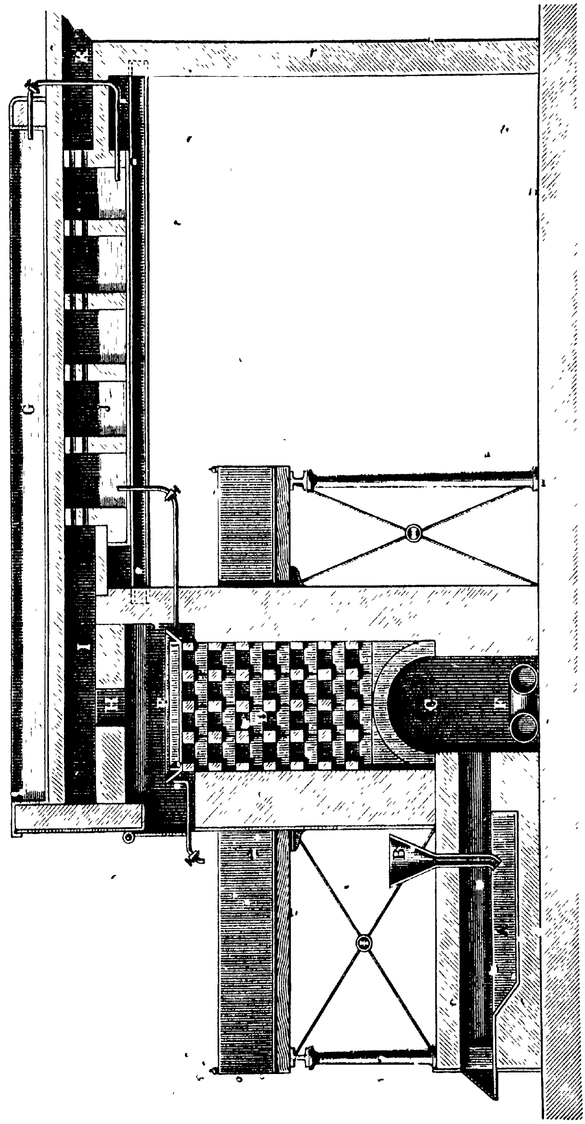


FIG. 71.

and the gases, now entirely deprived of free sulphur, pass away through H and the flue IK. On their way a platinum dish E, for concentrating sulphuric acid, is placed on the top of chamber D, and further (leaden) pans, J and G, are employed for a first heating of the acid. From here the acid gas passes into a Glover tower, where it is still hot enough to concentrate all the Gay-Lussac acid (equal to 1½ times the daily make of the chambers) up to 150° Tw., and impart to it a temperature of 127° to 132° C. The lead pans G J and platinum dish E produce daily 9000 lb. of acid of 91 or 92 per cent. H_2SO_4 from chamber-acid of about 123° Tw.; that is, two-thirds of the acid made from the 4000 lb. of brimstone burnt on plate A. Since this acid is taken directly from the chambers (the Glover-tower acid being used exclusively in the Gay-Lussac tower), and since the concentration is not driven to a higher point than 92 per cent., the platinum dish never requires any cleaning out of iron salts, etc.

Another sulphur-burner, on the principle of continuously supplying liquid sulphur, is that employed at the works of M. de Hemptinne, at Brussels, and shown in Figs. 72 and 73 (taken from the "Bulletin du Musée de l'Industrie de Belgique," January 1882, sent to me by the Author). It consists of a cast-iron arch A, strengthened by bracings, and resting on a large flanged wrought-iron plate with flat rivets, which can be heated or cooled by flues underneath. On this plate there are placed, side by side and as level as possible, four cast-iron plates with 3-in. upright flanges, intended for burning the sulphur, which is supplied by four spouts from a cast-iron box C, divided into four compartments and built into the front wall, as shown in the diagram. Perpendicular partitions D serve as lutes for preventing the burner-gas from blowing out in front; if the combustion should spread to the front, a cover (not shown here) would at once put out the flame. Thus the supply of sulphur takes place regularly; the four hinged doors, *a a*, in front serve merely for the entrance of the air and for clearing out the cinders. The arch A consists of ten pieces bolted together; it is covered by light sheet-iron shutters, E E, bent to the same shape and covered with a mixture of loam and straw, which can be raised or lowered by a chain, pulleys, and counterpoises. This admits of regulating the

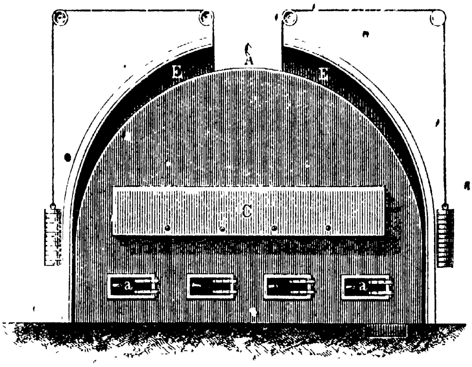
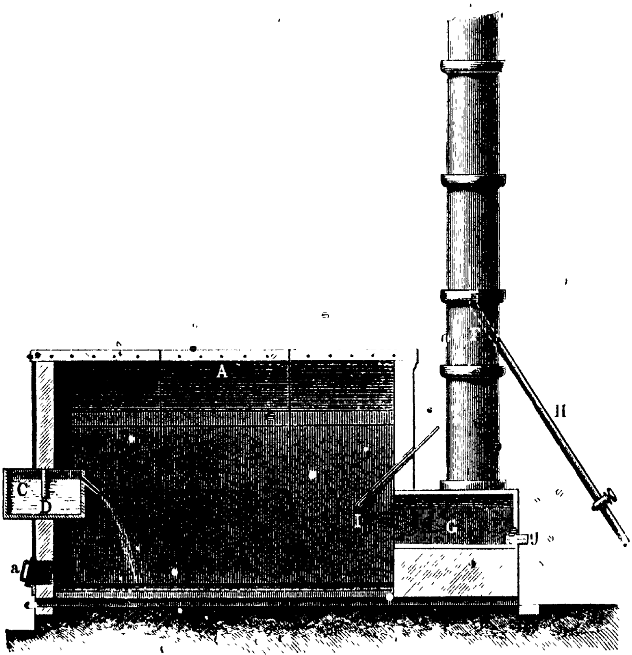


Fig. 72.



heat of the chamber; if it rises too much, one or more of the shutters, E E, are raised. An alarum thermometer I, in a copper tube, indicates the temperature. The gases escape through the metal pipe F, resting on a thick-walled cast-iron box G, from which the deposit formed can be withdrawn through J. Through H an extra supply of air can be let into the tube F. [This arrangement for supplementary combustion is decidedly imperfect.]

For producing cold and dry sulphur dioxide, free from sulphuric acid, such as is specially useful for preparing liquors for manufacturing wood-pulp, Némethy (Ger. P. 48285) recommends the combination of a sulphur-burner, cooled from the outside by water running down the sides, with a chamber, placed underneath, filled with iron borings in which the sulphuric acid is retained. From here the gas passes through a number of flat, perpendicular, iron boxes, cooled by water running down their sides, and then into the apparatus, where it is to be absorbed by milk of lime, etc.

W. Maynard (patented as a communication to A. M. Clark, No. 6982 of 1884) draws the gas out of the chamber where it is generated (by burning sulphur in cups) by means of a gooseneck pipe leading from the top of the chamber to a closed box provided with a funnel delivering into another box below. Water is discharged by a pipe into this funnel, which has grooved sides, so that the liquor running round as well as downwards forms a vortex, and draws away the vapours generated in the burning-chamber. This arrangement is evidently not intended for sulphuric-acid making, but for preparing a solution of sulphurous acid.

Brochon (Fr. P. 355252; *J. Soc. Chem. Ind.*, 1905, p. 1171) burns sulphur (or pyrites) with an excess of air under such pressure that the product consists partly of strong sulphuric acid, and even, under favourable conditions of SO_3, at least in the early stage of the process. The powdered sulphur (or pyrites) is blown through a vertical tube into a horizontal tube, narrowed to a small aperture, and removably fitted to the wall of a chamber. Air under pressure, say 10 atmos., is forced in through the horizontal tube, both from its bottom and from the end, supplying an excess of air. The vapours escape through a narrow channel at the farther end of the combustion tube into condensing vessels, or into ordinary lead chambers.

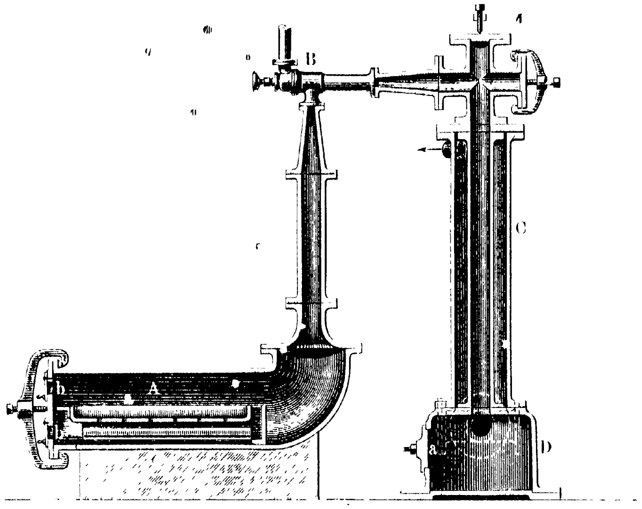


FIG. 74.

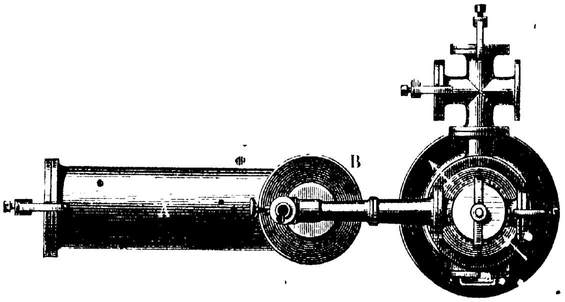


FIG. 75.

The following arrangement, by Korting Brothers, serves for preparing comparatively small quantities of sulphur dioxide from sulphur, for bleaching, in the manufacture of glue, for saturating the liquors in sugar-works, and the like. It is also used in wood-pulp works. A (Figs. 74 and 75) is a cast-iron retort provided with a perforated dish *a*, in which the sulphur is placed. B is a Korting's injector, made of regulus metal (5 lead, 1 antimony), which by means of a steam-jet aspirates air through the holes *b b* into A and causes the sulphur to burn. The vapours are forced downwards in the inner tube of the cast-iron cooler C, whilst cold water flows in the annular space between the two tubes, entering at the bottom and running out at the top. The box D, on which the cooler is mounted, serves for retaining any sublimed sulphur and other impurities. From here a tube leads the purified SO_2 to the place where it is to be utilised.

The Némethy burners, Korting burners, and others, are especially used in Germany and Austria for the manufacture of bisulphite of lime, to be employed in the manufacture of paper-pulp (called "cellulose") from wood. A number of other burners serving for this purpose are described in the *Papier-Ztg.* for 1894, pp. 1478 and 1830.

Fahrner (Ger. P. 183703) describes a burner for sulphur, fed by high-pressure air. The burner consists of a horizontal, cast-iron box, containing a perforated grid, upon which the melted sulphur drops, air being blown in at the bottom. The grid, which gets red-hot, and on which the gases and vapour are spread out, effects a complete combustion.

Marsden (for Paul and Tromblee, Amer. P. 749311) burns sulphur in a vertical revolving cylindrical retort, with longitudinal and transverse partitions, forming a chamber for the holding of a liquid mass, opening into an oxidising chamber; within which is arranged a melting-tank, connected by a pipe with the retort.

Blumenberg (Amer. Ps. 734397, 708512) describes a sulphur burner with the ordinary appliances.

F. A. Clayton (Ger. P. 194948) places on the sulphur burner a self-regulating valve for the admission of air, a little above the burning charge. One end of a pipe is fixed to one of the walls of the burner; the other end passes freely through the opposite wall and bears a plug, with a lever attached. A second tube is placed within the first and connected with it by a peg; asbestos packing fills the concentric space between the tubes. The inner tube is kept cool by a current of water. At its end, where it comes out of the outer tube, it bears the eye of a lever, in connection with the end of the outer pipe, and the other end of this lever is connected with the air-inlet valve. The outer pipe expands by the heat of the burning gases, while the inner pipe remains much as before; the movement, caused by the expansion of the outer pipe, communicates itself to the lever and thus to the air-valve. Hence, if the temperature of the burner reaches a certain point, air will enter into the upper part, or else the inner, water-cooled pipe is placed somewhere else below or outside the burner, and the expansion of the furnace bottom itself is utilised for bringing the aforesaid valve into action.

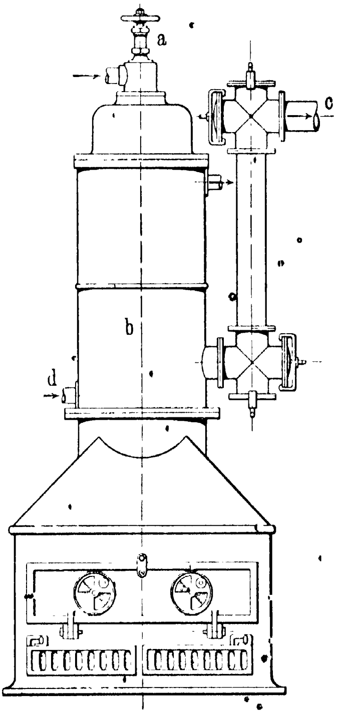


Fig. 76.

The Schutte and Koerting Co. in Philadelphia supplies a sulphur furnace, shown in Fig. 76, made entirely of cast-iron. The lower part contains a pan in which the sulphur burns. A steam-jet exhauster *a*, draws the gas through the cooler *b*, placed above the pan, and discharges it under pressure of about 10 lb. of water through the outlet pipe *c*. As the exhauster creates an inward suction, there is no escape of smelling gases from the furnace. The object of cooling the gas (*d* shows the water inlet) is to protect the exhauster (which is partly made of lead) and to prevent the gas from reaching the saturating-tanks at too high a temperature. By taking off the top-cap, the exhauster and the whole apparatus is accessible for cleaning and renewals. This furnace is made in three sizes for burning 10, 20, or 40 lb. of sulphur per hour, and is specially intended for the manufacture of sulphites.

O. N. Witt (Ger. P. 185332) proceeds as follows, in order to avoid in the burning of sulphur the formation of flowers of sulphur, which means both a loss and trouble caused in the acid-chambers through a skin of sulphur covering the acid and preventing its contact with the chamber gases. For this purpose the sulphur is first melted and then issues through a circular tube, surrounded by a second tube through which passes steam or air under a pressure of several atmospheres. This converts the issuing sulphur into a cloud, consisting of microscopically fine droplets, which on burning yields SO_2 completely free from sulphur vapour. If that cloud is not lighted, but passed into cooling-chambers, an exceedingly fine powder of sulphur is obtained.

Savage (Amer. P. 841576) describes a sulphur burner, rocking on a fixed base.

The Chemische Fabrik Schering (Ger. P. 191596), for the continuous burning of sulphur in air or oxygen, employs a furnace, surmounted with a dome, in which a sieve is moved backwards and forwards in a horizontal direction. The sulphur, in the state of powder, is introduced in a regular way, and below the sieve meets air, blown in by a pump, where it at once burns; part of it passes into the state of vapour, but this is also burned in the furnace, which is filled by a "sea of flame," so that the oxygen is quantitatively converted into SO_2.

Tufts (Amer. P. 891115) introduces into a furnace for burning sulphur the gases obtained from a pyritic smelting furnace, after passing them through a dust separator, and thereby effects concentration of the SO_2 and equalisation of the temperature.

Lyman (Amer. P. 911735) attains the complete combustion of brimstone by running the melted S, together with air, into a chamber, so that the S is converted into spray and intimately mixed with the air.

The Sachsenburger Maschinenfabrik (Ger. P. 196371) describe the sulphur-burner shown in Fig. 77. The sulphur is introduced at *i*, and ignited through the opening *n*, air being supplied by pipe *a*. The SO_2 escapes by pipe *b*, and molten sulphur collects at the bottom of the furnace. Fresh sulphur is introduced through *e* into the funnel *f*, the lower end of which is luted by the molten sulphur in *c*. The upper portion of the funnel is water-cooled by the tank *o*. Compressed air may be introduced into the pipe *b*, to burn any sulphur sublimed there.

Clark (Amer. Ps. 952098, 952099, 952100) admits hot air into the sulphur-burner, in order to effect the combustion of any vapourised sulphur, and keeps the gases at about 1100°, in order to decompose any SO_3 that may have been formed. His furnace comprises a preliminary combustion chamber, and a second combustion chamber into which the products from the first chamber are directed. Means are provided for the admission of hot and cold air, and for the regulation of the furnace temperature.

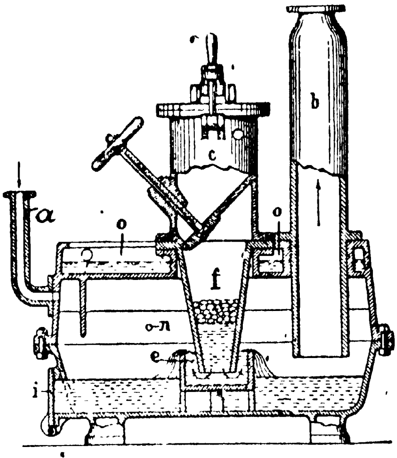


Fig. 77.

Grimm's sulphur-burner (B. P. 10774 of 1909; Amer. P. 957418) consists of a combustion chamber suspended in the upper part of a metal jacket, through which water is made to flow. The sulphur is contained in a loose tray, slightly raised above the floor of the chamber, and air is supplied under pressure. The gas passes out of the furnace and then back through a number of cooling-pipes situated in the lower part of the jacket; any proportion of air may be mixed with it by means of a valved by-pass from the air-supply pipe. Molten sulphur may be supplied as required from above by means of a screw valve. The supplies of air and sulphur are thus under perfect control, and any desired temperature may be maintained, gas of any desired concentration being continuously produced.

Westgate's burner (B. P. 17348 of 1909) is very similar to the preceding.

Contamin (Amer. P. 996215) employs for the production of SO_2 for fumigating, etc., a combustion-chamber containing superposed plates to hold the burning sulphur and baffle-plates to give the gases a zig-zag course through the chamber; then follows a chamber with cooling-pipes around which the gas flows; from this the gases pass through a pipe with reticulated terminus into a dust chamber, provided with baffle-plates, from which they are taken by means of a pump into a refrigerating-chamber containing baffle-plates and cooling-pipes.

Oddo (B. P. 21255 of 1908; Ger. P. 225321; Fr. P. 397450) describes brimstone burners, similar to the Malétra and Herreshoff burners for pyrites smalls, both for operation by hand, and in circular mechanical furnaces with four stories, provided with a vertical spindle with radial rotating arms.

He discusses his processes for utilising raw brimstone ores directly for the manufacture of sulphuric acid in *Chem. Zeit.*, 1910, pp. 505-507, 514-515.

Stebbins (Amer. P. 934700) supplies fused sulphur to the burner automatically and continuously, without opening the front door, which always causes irregularities in the entrance of air. The proper quantity of air is constantly introduced, and a mixture of SO_2 and air of perfectly constant composition is produced.

Thalin (Norw. P. 20450) burns sulphur vapour with the requisite quantity of air in a revolving drum; the non-oxidised sulphur vapour is precipitated in a special chamber and burned.

G. E. Miller (Amer. P. 1018255) provides brimstone burners with an automatic feeding arrangement, and with a mechanical agitator operating beneath the surface of the burning sulphur.

Feld (B. P. 21996 of 1911) burns the sulphur in two phases. In the first place, only so much air is introduced as is necessary to produce a sufficient degree of heat. The mixture of sublimed sulphur with SO_2 thus obtained is completely burned into SO_3 in a current of preheated air.

In Germany, in 1900, thirty-three paper-works made sulphite cellulose (wood-pulp) by means of brimstone, of which they consumed 15,000 tons per annum, whilst other thirty-three works employed for that purpose 70,000 tons pyrites. Both kinds of works together produced 350,000 tons of wood-pulp per annum.

In the United States that industry is also very largely developed.

Residue from Brimstone-Burners.

The following analysis of the *residue from the sulphur-burners* has been made by Richardson (Richardson and Watts, *Chemical Technology*, vol. i, part 5, p. 198):—

Sodium sulphate[1]	13·77
Calcium sulphate[2]	28·49
Calcium silicate[2]	15·91
Sodium silicate	1·10
Ferric oxide and alumina	2·80
Water and sulphuric acid[1]	13·05
Insoluble	24·29
	99·41

Cooling the Gas from Brimstone-Burners.

A special cooling of the gas from sulphur-burners for manufacturing sulphuric acid (as distinct from that of bisulphite of lime) is, as a rule, not only unnecessary, but even injurious; so that, for instance, in the furnace shown in Figs. 62 to 65 (pp. 396, 397) the vertical metal pipe conveying the gas to the chamber had to be protected against cooling by a brick jacket. Even where no cooling takes place by water-pans, steam-boilers, etc., the gas gets into the draught-pipe sometimes at only about 100° or 120° C. temperature, which is just sufficient not to allow the nitric acid to condense before it gets into the chambers, a contingency decidedly to be avoided. Where water-tanks, acid-pans, etc., are used, the temperature of the gas is said to come down as low as 40° C.; in this case only liquid nitric acid can be used for the chambers. In Blair's or Glover's continuous burner the temperature certainly rises much higher; and in this case a cooling arrangement, such as that described, was formerly thought indispensable, before means had been found of utilising the heat of the gases in a Glover tower or otherwise. In the preceding descriptions of other recently constructed burners the cooling of the gases is several times mentioned.

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[1] The sodium sulphate and the free sulphuric acid (or rather the acid sulphate) evidently come from the nitre-pots boiling over.

[2] The lime no doubt partly comes from the brickwork of the furnace.

B. THE PRODUCTION OF SULPHUR DIOXIDE FROM PYRITES.

1. BREAKING THE PYRITES.

The pyrites, as it comes into the market, is always sufficiently pure to make a separation from gangue unnecessary, except in the case of pyrites picked from coals ("coal-brasses," p. 65); but this is only a locally used by-product.

It is, however, always necessary to break up the larger lumps in order to burn the pyrites completely; and this is always done at the works themselves—except in a few cases, where they buy smalls direct from the mines. The majority of the factories break the ore by hand; and it is found that various descriptions of ore behave very differently in that respect. The Norwegian ore is the hardest; here the large lumps have to be broken with great labour by means of 20-lb. forehammers. The Westphalian ore is much more easily broken—still more easily the Spanish and Portuguese and some of the French ores; these, however, make a good deal more smalls, 10 per cent. and more. The softest ore is that from Chessy, consisting of loosely aggregated individual crystals, which by a blow of the hammer fall to powder. Some of the Spanish ores are equally roughly crystallised; these ores are very troublesome for use as lumps.

In England the ore is generally broken so that all the pieces pass through a sieve with 3-in. holes. On the other hand, as few smalls as possible are made. The broken ore must be sifted again to separate the smalls, for which purpose some works pass it through a ½-in., others through a ¼-in. riddle. What remains on the riddle is *lumps*; what passes through, *smalls, fines* or *dust*. Each of them has to be treated separately. It is very important that the ore be used neither in too large nor in too small pieces. In the former case it does not burn right through; there remain green cores in the interior of the cinders, which can be seen on breaking them up. These large lumps also get too hot on burning, and may cause the formation of slags (scars) by production of FeS, as will be subsequently explained. If, on the other hand, the pieces are too small, they prevent too much the access of air, and similar results follow in this as in the former case.

It is quite obvious that the pyrites burners can be worked to full advantage only if the ore is in pieces of as uniform size as possible, and it would hence be the best plan, although it is hardly practicable in reality, to separate the broken ore into a number of sizes to be burnt in separate kilns. At Oker formerly the ore was broken to walnut size for the grate-burners, as shown later on. For deep kilns, as now altogether used there, the ore is broken into pieces of 2½ in. size. The fines, sifted through ¼-in. sieves, are burned in a Rhenania blende furnace (*cf.* later on).

Owing to the great manual labour required for the breaking of pyrites, *mechanical stone-breakers* have been introduced for this purpose, quite similar to those which are used for road-metal. One of these machines is that of Blake, built by Messrs Marsden of Leeds, which is shown in Figs. 78 and 79. This machine is made of various sizes, and accordingly varies in the amount of work turned out and in the size of stones it can attack. A and B are the two active parts, the "jaws." A is fast and perpendicular, B movable, and makes with A an angle of 72°, by oscillating a little round the fixed shaft D. This movement is communicated to the jaw B from the main shaft, H, by means of the angle-lever, EE', and the crank motion, GH, so that the angle-lever presses the jaw B against the stones charged, the return motion of B being caused by a spring, F, cased in india-rubber. The angle-lever is adjustable by the wedge, N, lying behind its arm E'. The roller, C, causes the broken stones to be regularly ejected; it receives its motion by a belt from the main shaft, by means of the pulleys, K, L, and the expanding roller, M. The crank-shaft, H, is also driven by a belt from the fast and loose pulleys, H'. The machine is mounted on a four-wheeled bogie. It makes a great deal of noise and needs frequent repairs; but the jaws, which principally suffer, are so arranged as to be easily replaced.

Blake's engine has been improved by Broadbent & Son, of Staleybridge, who have replaced the spring bedded in india-rubber by a simple, easily-adjustable lever arrangement, which saves labour as compared with the original contrivance. Output, according to size, from 40 to 130 tons in ten hours; price £140 to £375.

At Oker, a steam-engine of 12 h.p. drives two stone-breakers,

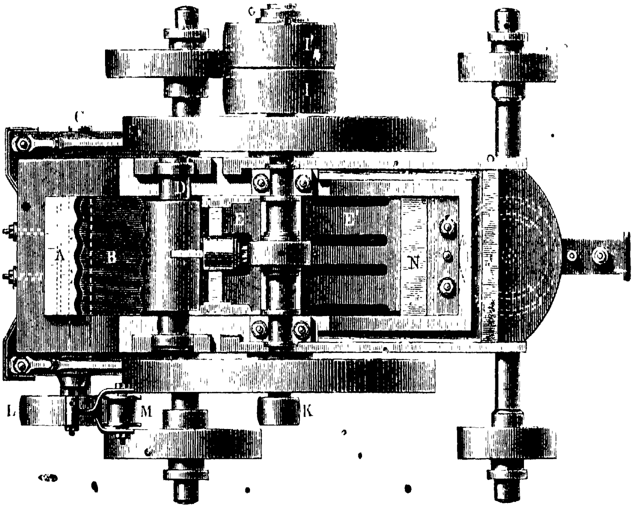

FIG. 78.

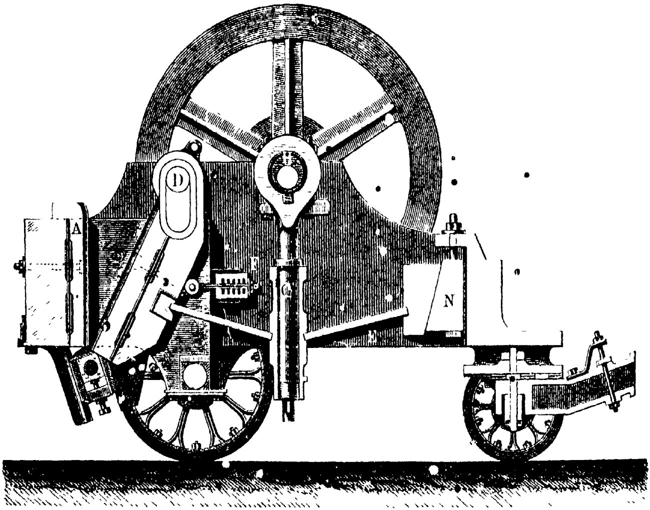

FIG. 79.

mounted one above the other. The higher one breaks the large stones roughly, the lower one down to the proper size. They supply, in the case of very hard ore, of 2½ in., 60 tons, with milder ore, 72 tons per shift of ten hours.

A crushing-mill was invented by Motte, at Dampreny, near Charleroi, which has been improved by the Markische Maschinen Fabrik (Ger. P., 16th October 1887; *Dingl. polyt. J.*, ccxxvii. p. 58). The principle is that of a peculiar kind of mortar, with hollow bottom, in which the crushing is done by a pestle, as seen in Fig. 80. Whether this mill is really preferable to the older stone-breaking machines, experience will show.

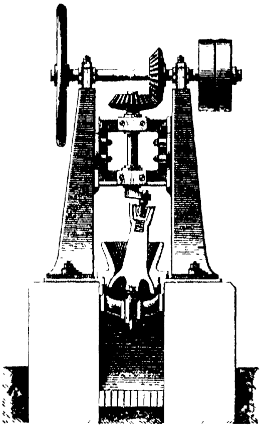
FIG. 80.

Durand and Chaptal's stone-breaker consists of a number of hammers attached to a horizontal revolving shaft. It is said to make less dust than other stone-breakers. The smallest apparatus breaks from 8 to 25 tons of stone in ten hours, with an expenditure of 2 or 3 h.p., the larger size from 80 to 130 tons, with 6 h.p.

Vapart's breaking-mill (address, "Chênée, Vieille Montagne") works centrifugally.

The Humboldt Engineering Co. at Cologne (Ger. P. 1906, 12th January 1878) manufacture stone-breakers which do twice the work of those formerly in use, with the expenditure of the same force.

Other improvements in stone-breakers have been invented by Brown (*Scient. Amer.*, 1879, p. 194) and Welter (Ger. P. 7494, 5th March 1879).

A machine very much recommended is Breuer's "Sectorator" (Ger. P. 30477) supplied by Ernst Maetz, Berlin, S.W. As shown in Fig. 81, it contains a straight breaking-jaw, *a*, firmly connected with the solid frame, whilst the movable jaw, *b*, is suspended in two steel trunnions, and is partially revolved against the jaw, *a*, thus crushing the material. The angle between the two jaws is rather acute, so that large pieces are easily caught and carried forwards towards the bottom slit. If both jaws are arched, the material, especially large pieces, would be able to escape upwards for a long time, until gradually broken up. The width of the bottom slit is adjustable by a wedge even during work, so that any size can be obtained. The plate *c* behind the excentric sheave, which is easily exchanged, is of cast-iron and of a smaller section than any other part of the machine subjected to a breaking-strain, so that in case of excessive strain by the passage of a foreign body (iron, etc.), that plate must give way before any other part of the machine.

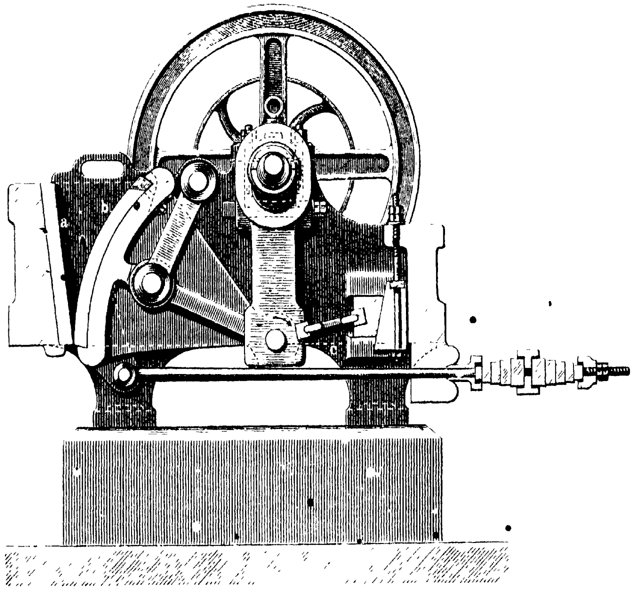

FIG. 81.

Even at some large works they prefer dispensing with mechanical stone-breakers, principally for two reasons. The first of these is that they make more dust than breaking by hand; but since dust is now even more profitably burnt than pieces, this reason is no longer valid. The other reason is, that at large works there is always a certain number of men who are incapacitated for other work or who are temporarily unoccupied, and these are best set to stone breaking.

2. PYRITES-BURNERS FOR LUMPS.

Among the apparatus for burning pyrites in the manufacture of sulphuric acid, a distinction has to be made between those intended for lumps and those intended for smalls. It is indispensable to keep both kinds apart, and to employ different apparatus, or at least processes, for them; for if the broken ore is put into the burner without separating the smalls, the air-channels, which ought to remain between the pieces, are soon partly stopped up with powder, and the access of air becomes irregular; thus scars are formed and proper work is then impossible. Apart from the coarser and finer powder obtained on breaking, a great deal of smalls comes into the trade direct from the mines, obtained there by the use of water for separating the ore from the gangue.

Where cupreous pyrites is roasted without any regard to the utilisation of the sulphur, the only object being the extraction of the copper, usually no regular kilns are employed at all, but the ore is burnt in "heaps." This was formerly done on an enormous scale in the south of Spain; but the damage to health and vegetation was so great that a law was passed compelling manufacturers to abate this nuisance. In order to avoid the necessity of building the very large number of closed kilns which would be required for that purpose, various proposals have been made. We quote that of Fleming (B. P. 10153 of 1887). Above the roasting-heap, and extending downward over the whole portion (about one-third) which emits the fumes, is suspended an iron hood, lined with tar and painted outside with a non-conducting material. The hood is supported by chains from two pairs of shear-legs, and the whole is strengthened by iron stays. At one end of the hood is a pipe, by which the roaster gases are led to condensing-flues, where arsenious acid separates out, and thence into vitriol-chambers. If the gases contain an excess of air, they are taken through calcining-furnaces; if the amount of air is insufficient, more can be supplied by regulating-dampers in the flues. [Apart from all other objections to this process, the "iron hood lined with tar" is sure to be not very durable]

The burning of pyrites in lumps (pieces) for the manufacture of sulphuric acid is always done in such a way that the combustion heat of the pyrites is utilised for maintaining the process without employing any extraneous fuel. The apparatus used for this purpose are called "kilns" or "burners." In the first edition of this work (pp. 151-154) there will be found a description of the old and now abandoned kilns, with many diagrams—as the burner originally employed by Farmer, the first shape of tall kilns without grates, the Oker kilns for roasting the Rammelsberg ores. These kilns (except Farmer's) are constructed without grates; they are still used for roasting poor ores, lead-matte, etc. In the same edition there is a description of the Belgian hearth-furnaces and of the Marseilles furnaces, both of them very faulty and quite antiquated (pp. 157 and 158). This also holds good of the various descriptions and illustrations of "Freiberg kilns," still given in our second edition (pp. 214-218). Instead of these, I am enabled, through the kindness of the respective authorities, to show the kilns now used at Freiberg and at Oker, at the Government works carried on at those localities.

For poor ores and intermediate products which must be treated at metallurgical works (pp. 112 *et seq.*), furnaces are required of a different kind from the grate-burners now universally employed for good pyrites in lumps. The style of kilns now used at the Muldenhutten near Freiberg is shown in Figs. 82, 83, 84. They serve for poor iron-pyrites containing blende and arsenical pyrites, as well as for lead- and copper-matte.

The grate formerly employed at Freiberg has been replaced by slanting cast-iron plates, *g*. The air does not now enter through special channels, but through the discharging and working holes. *a* shows the charging hopper, *b* the channel through which the charge gets into the kiln, *c* the exit channel for the roasting gases, *d* openings for spreading out the charge, *e* working-holes, *f* discharging-holes. Each kiln roasts about 25 cwt. of pyrites per twenty-four hours; 5 kilns are combined in a set. The sulphur is roasted off to 4 or 5 per cent. left in the cinders.

For richer and purer pyrites, at Freiberg grate-burners are employed, consisting of 3 kilns, with 25 sq. ft. grate surface each, and a distance of 4 ft. from the movable grates to

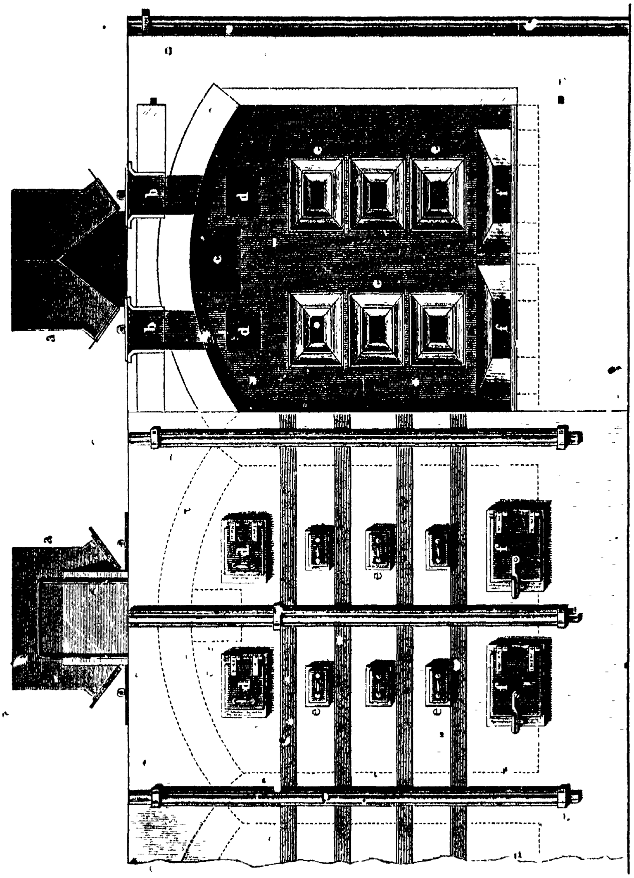

FIG. 82.

the crown of the arch. Each set roasts about 36 cwt. pyrites per twenty-four hours down to 2 or 3 per cent. S.

The kilns used at Oker are exactly like the Freiberg kilns just described. They are of two different sizes—deeper kilns (with a layer of ore 9 ft. deep) serve for the poorer ores,

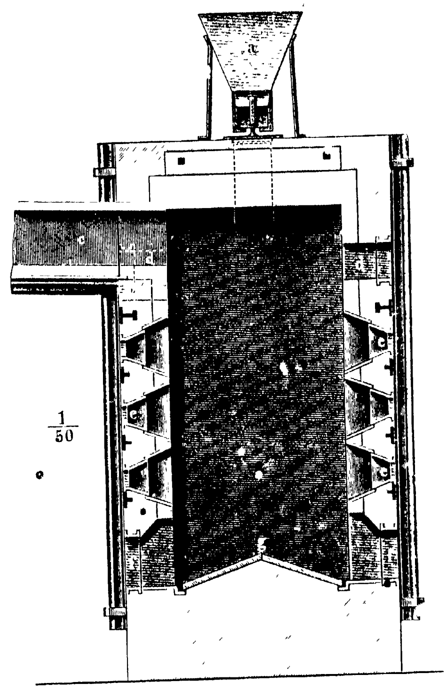

FIG. 83

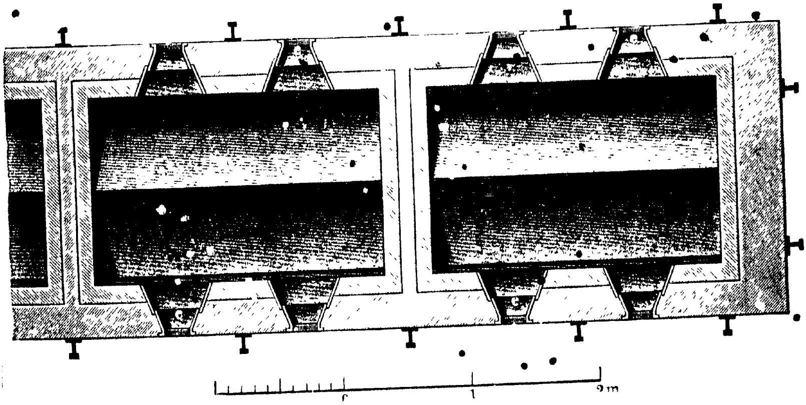

FIG. 84.

shallower kilns (the ore lying 6 ft. deep) for the richer ores (described, p. 115). The English grate-burners, formerly employed at Oker, have not been found suitable for this class of ores.

Kilns of the just-described kind have been found indispensable for roasting poor ores, matte, etc., where the sulphuric acid is a by-product and where the heat generated in the process is less than when roasting ordinary pyrites, containing at least 40 per cent. sulphur, usually a good deal more, such as is now universally employed for the manufacture of sulphuric acid as a principal product. For such richer ores the kilns or burners ought always to be constructed with *grates and ash-pits.* This causes a considerable improvement in the working of the furnaces. Where the air has merely to pass through a mass of burnt ore, its quantity cannot possibly be regulated at the inlet, but only by dampers at the other end of the furnace. It is even a more serious disadvantage that in this case the subdivision of the air inside the burner must be very irregular. According to the greater or smaller resistance offered by the individual portions of the layer of pyrites, the air will pass through very unequally, and in less quantity at the places where most pyrites is lying and where it is most required. The introduction of a grate and a closed ash-pit alters the state of the case at once, in this way, that only a definite quantity of air need be admitted into the ash-pit, and that, moreover, this air must first spread equally underneath the grate and rise all over the area of the burner. Thus the ore is much more completely burnt, and at the same time richer gas is obtained, which leads to a better chamber-process, higher yield of acid, and smaller consumption of nitre; the operation of drawing out the burnt ore becomes much more regular and offers a greater guarantee against raw ore getting into it; lastly, it does not happen so often that fused masses ("scars") are formed in the burner, although also in the case of grates this easily happens if the method of working is faulty.

The introduction of grates led to further improvements—to begin with, a diminution of the height of the burners, which made them much handier for working, and which acted especially well with more easily fusible ores, although in some places the other extreme of too low layers of pyrites has been resorted to.

The different descriptions of grate-burners which were introduced into England about 1860, and have been employed up to this day both there and in many factories abroad, are shown in Figs. 85-89.

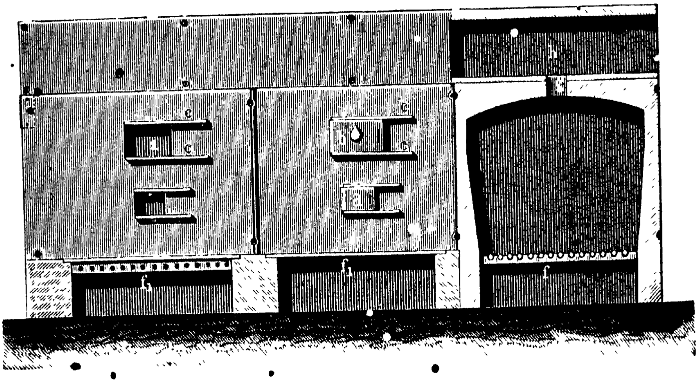

Fig. 85.

Figs. 85, 86, 87 show a somewhat simple construction, which can be made with open sand-castings; Figs. 88 and 89 a more expensive kind of front plates, requiring planing,

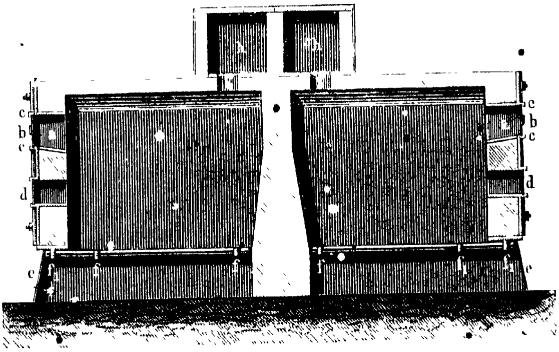

Fig. 86.

turning, etc.: the latter are much neater and cleaner, because no putty is required for the doors. Sometimes these front plates, however, become a little warped, and then the doors are not tight without putty.

Fig. 85 shows two burners in front elevation and one in section, the first burner without doors. Fig. 86 is a cross section, showing two rows back to back; Fig. 87 a sectional plan, half taken just over the grate, half through the middle of a door. *a* is the working-opening, with the door *b*, which slides in the grooved ledges, *c c*, provided on the front plate. The small door *d*, only to be used exceptionally, is arranged in precisely the same way. The openings of the brickwork inside are protected by small metal plates; *e* is the movable cover of the ash-pit, provided with air-holes; *f f* are the grate-bearers; the front bearer, *f*, at the same time carries the bottom plate for the front wall, and is perforated with round holes; while *f f* are cut out in semicircles. The arches are sprung parallel with the working-doors, and by the draught-holes, *g g*, are in connection with the gas-flues, *h h*. The latter, like the burners, are cased in metal plates; they are covered with fire-tiles.

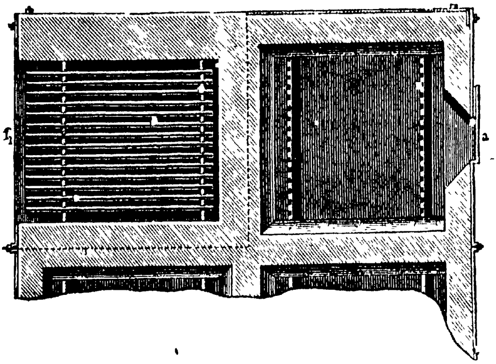

FIG. 87.

A somewhat more costly but more perfect arrangement is shown in Figs. 88 and 89, in front elevation and two sectional elevations. *a* is the working-door, with the small slide *b* for observing the interior of the burner; it turns on hinges, and, as shown in Fig. 88, lies on a projection of the front plate, slanting forward towards the bottom; all the metal parts coming into contact are planed and faced, so as to close air-tight. The doors *c c* for the grate and *d* for the ash-pit are constructed in the same way, whilst the rarely-used doors *e* and *f* (the latter for the gas-flue) are made in the simple manner shown in Fig. 86. The burners are supposed to be the last of the row; so that the nitre-oven *g*, with the semi-cylindrical trough *h*, the saucer *i*, and the hopper *k* are immediately joined to them. The diagrams are all on a scale of 1 to 50.

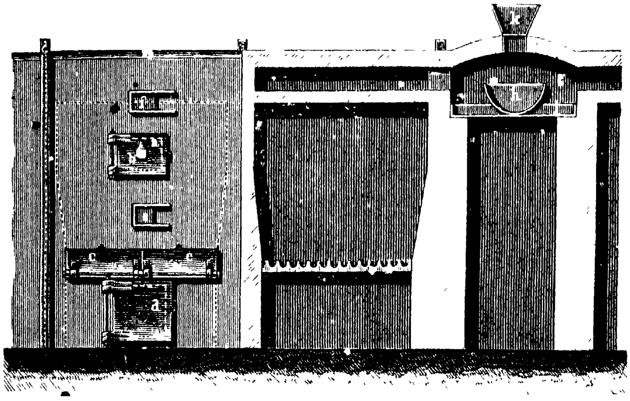

FIG. 88.

English pyrites-burners generally have a moderate area of grates, about 4 or 5 ft. wide, and 4½ to 6 ft. from front to back. The inner walls sometimes rise quite perpendicularly; more frequently the two sides and the back slant a little outwards, up to the level of the working-door, to the extent of 6 or 9 in. in width, and half as much in the back; from that level the walls rise again perpendicularly up to the roof. The front wall, which is only 9 in. thick, and mostly protected by a 1-in. or 1½-in. metal

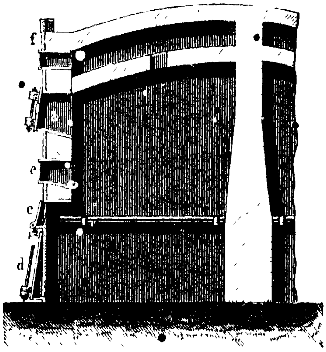

FIG. 89.

plate, rises perpendicularly, and is perforated by several working-holes. The ash-pit has either vertical sides or, more rarely, sides converging towards the bottom, in order to facilitate the removal of the cinders. Its depth varies from 16 to 24 in. The level of the working-doors, which determines the depth of the layer of pyrites, varies from 1 ft. 8 in. to 2 ft 6 in.; but the former depth is considered by most English acid-makers too little, at any rate for average ores, and they prefer a depth of between 2 ft. and 2 ft. 4 in., but nearer the higher than the lower limit. In Germany, the depth of ore is only 1 ft. 6 in., even down to 1 ft. 4 in. (*cf.* p. 434). The reason for this is the fear of scarring, which English experience with the same ores proves to be unfounded. The height from the upper level of the ore or to the abutment of the arch is usually about equal to that of the working-door, say 9½ to 12 in., and from there up to the crown of the arch another 8 or 9 in. The arch itself is either sprung from side to side, as is the custom on the Tyne (whereby the walls are made to bear the weight more equally and the working through the doors is facilitated), or, as is usual in Lancashire, from front to back (which is more advisable in the case of two rows of burners being built back to back, in which case the arch is sprung over both burners together, with a supporting wall in the centre). In any case it is advisable to build the burners back to back, even with arches sprung from side to side, wherever it is locally possible; thus one back wall is saved, the heat is kept up better, and a common gas-flue can be employed.

The *gas-flue* of the English burners is always at the top, each burner-arch having a hole of 4 to 5 in. square leading into it. These holes are not always provided with dampers; but by gradually increasing the size of the holes as the distance from the main shaft becomes greater, regularity of draught is produced. The flue itself can be made of bricks set in tar and sand, and covered with fire-tiles. Most modern works prefer forming it by a second arch, about 6 or 12 in. above the burner-roof, reaching right across the whole burner, and supported by the front plate being made high enough.

The principal feature of the English pyrites-burners, which is found in all continental works as well, except in some burners for metallurgical purposes (Mansfeld or Freiberg kilns), is the employment of *grate-bars* of square or oblong section, movable in bearings, and leaving larger or smaller spaces between them, according to their position. (According to Hasenclever, in Hofmann's *Ber.*, 1875, i. p. 158, movable grate-bars have been used in France ever since 1848.) Fig. 90 represents such a grate-bar, showing also the parts which are forged or cast with a circular section, so that they can easily turn in the respective hollows of the bearers. Bars 2 in. square are usually made of wrought iron; the oblong bars, 2 by 3 in., which, being turned on edge, leave a larger space, and therefore only suit

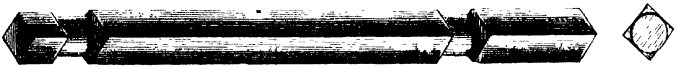

FIG. 90.

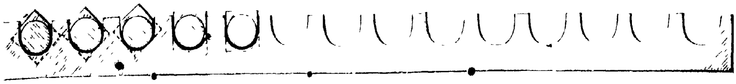

FIG. 91.

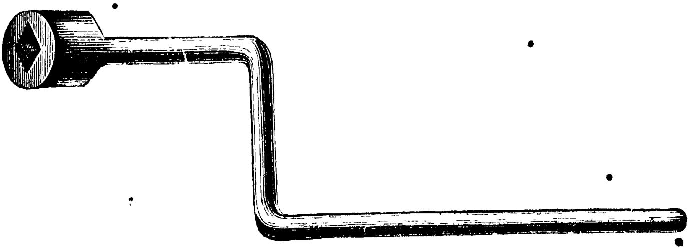

FIG. 92.

larger pieces, are mostly of cast iron. The grate-bars rest on cast-iron bearers, as shown in Fig. 91; in the shallower kilns (4½ to 5 ft. from front to back) there are two such, in the deeper kilns (5 ft. 3 in. to 6 ft. from front to back inside) three. According to this, of course, two or three rounded places must be made on the bars themselves. Lest these should be weakened too much, the diameter of the round parts in the square bars is made equal to the side of the square, in the oblong ones equal to the smaller side. In any case the front piece of each bar, where it projects beyond the bearing-bar, has a square or oblong section, so that it can be turned round its axis by means of a suitable key (Fig. 92). The intervals between the grate-bars are mostly managed so that with 2-in. bars they are about 2 in. when the bars are in the situation shown in Fig. 93; but if they are turned 90°, as in Fig. 94, the intervals will only amount to 1¼ in. In another actual instance the diameter of the bars was 1¼ in., the clear distance in the straight position 1½ in., in the diagonal position 1 in. If, lastly, the situation is as in Fig. 95, where half of the bars are turned, the intervals will be between the two above limits; and as each bar can be turned separately, many combinations can be produced. Usually the bars stand as in Fig. 94—that is, all with their diagonals in a horizontal plane, or with the smallest possible intervals, so that the pieces of ore cannot fall through. As soon as a portion of the ore has to be removed, the attendant takes hold of the front end of the bar with his key, and moves it a few times from side to side. Thus a kind of crushing action will be exercised on the cinders getting between the two bars, the intervals are momentarily enlarged, and the cinders jammed between the bars are forced downwards. Of course great bodily exertion is required for this work. At the same time, by the action of the key, the pyrites is loosened up to a certain height. The workman now goes from one bar to another, generally leaving one out, and shakes them, according to his judgment, so far that an equal quantity of burnt ore is drawn out all over the area of the grate. That which has fallen through is allowed to lie in the ash-pit till the time comes, once every twenty-four hours, for opening the bottom door and taking away the cinders.

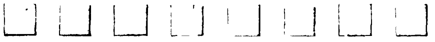

FIG. 93.

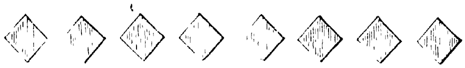

FIG. 94.

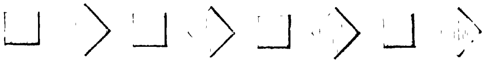

FIG. 95.

A new shape of bars, which was said to possess great advantages over the ordinary angular ones, was patented by W. Helbig (*Dingl. polyt. J.*, ccxxvii. p. 67) and is shown on p. 222 of our second edition, but omitted here, as it seems to have found no practical application. It was a cast-iron bar with a worm-thread all round it.

A burner patented by Harlan & Grenshaw (Ger. P. 100243) contains hollow grate-bars, with tapering, narrow chambers, rising vertically nearly to the top of the layer of pyrites, so that the air enters not merely at the bottom above the grate, but also higher up, nearly to the top of the pyrites.

Dr Burgemeister (private communication) employs bars made of a cruciform section. When turning these round, the smaller pieces easily fall through; the larger lumps get between the bars and either pass through on turning back or are crushed. The following diagram shows the different positions of the bars:

+ + + +
× × × ×

It is a great improvement (but rarely met with, because it necessitates a somewhat complicated plant) if the *ash-pit* is deep enough for introducing an iron bogie below the grate whose top equals the whole surface of the grate in size; the ash-pit door, of course, must be correspondingly large. The cinders in that case fall direct into the bogie, and can be wheeled out in a few moments; otherwise they have to be raked out by hand, during which time the door must stand open, and much false air gets into the burner. Where there are not two rows of burners built back to back, it is possible to charge on one side and discharge on the other; but there is not much advantage in this arrangement, which takes a great deal of space.

The *discharging of the burnt ore* (*cinders*) is sometimes expedited by iron bogies running on tramways, which are introduced into the ash-pits, and into which the cinders fall when the grates are shaken. This very good plan necessitates a system of tramways and turn-tables, as well as a lowering of the whole floor. The following simple and equally efficient plan seems therefore worthy of recommendation. It is a *tilting-box* (Figs. 96 and 97). There are two independent parts:—first, an iron box, of suitable dimensions, with two outside pivots near the upper edge; secondly, a light but strong wheeled frame, which ends in forks fitting under the pivots. As shown in the diagram the whole is used like an ordinary iron wheelbarrow on any hard ground. But by lifting up the handle the box is first lowered to the ground, then the forks slip out and the frame can be run back. Similarly, the box is taken up

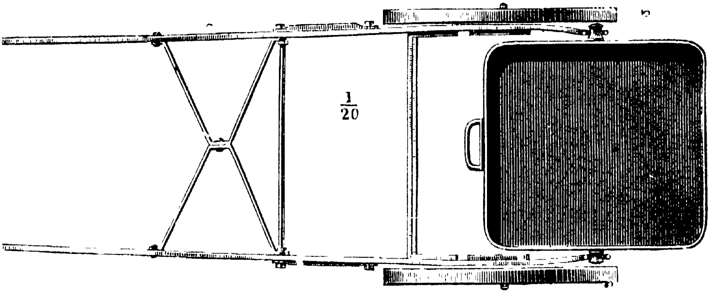

FIG. 96.

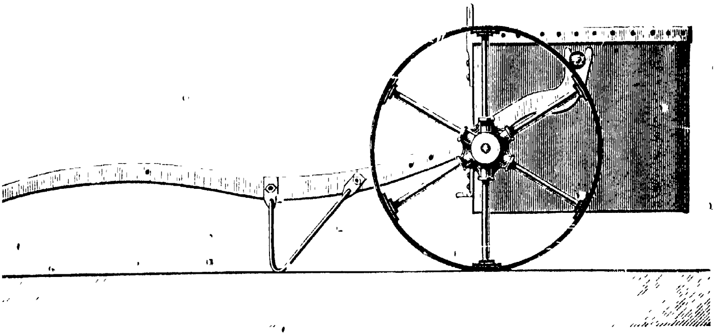

FIG. 97.

again by running the frame in, and depressing the handles till the forks take hold of the pivots. The boxes can be made to fit into the ash-pits, and the cinders discharged into them directly from the grates. Of course other applications of this barrow will be found useful in chemical works.

In order not to be obliged to open the whole ash-pit when shaking the bars, all the best furnaces are provided with a slit in the front plate, through which the ends of the bars are accessible. Except whilst the bars are being shaken, the slit is covered by a door, which is best made in two halves.

Special arrangements for preventing the blowing-out of sulphurous gases.—Norrington (B. P. 4131 of 1878) makes the ash-pit doors to slide in horizontal frames, and connects all the doors of a set of burners by jointed rods, so that they can all be moved together in a horizontal plane by means of an endless screw and gearing at one end. All the ash-pit doors are thus opened and shut at the same time. This is always done whenever any one of the working-doors is opened so that no gas can blow out, as the air cannot enter in any other way. According to information from Messrs Charles Norrington & Co, Plymouth, this arrangement effects a considerable saving of nitrate of soda and of sulphuric acid; owing to the regularity of draught, all kilns burn equally well. This statement is confirmed by Dr Ballard (Report to the Local Government Board, 1879, p. 180).

According to a communication from Mr K. Walter, a simple means of preventing the blowing out of gas at the working-door during charging is this: to arrange a flue underneath the burners, in connection with the chimney, which is opened during the charging just sufficiently to prevent any blowing out at the working-door. Less gas is lost and less nuisance is produced in this way than is otherwise the case from the working-doors. With this arrangement the ash-pits require only loosely put-on wrought-iron doors.

In England it would probably not be allowed to discharge the gas into the chimney, even for a short time: this objection is overcome by the following plan:—

Hasenclever (*Chem. Ind.*, 1895, p. 494) describes the following arrangement for preventing any escape of gas from the burner-doors into the working-shed during the time the doors are open for charging. In some cases the chambers are placed high enough over the burners (say, at least, 18 ft. above the floor) to secure sufficient draught at all times; but even then the false air entering during the time of charging may be troublesome in the lead chambers. The device proposed by Jurisch (*Ueber die Gefahren für die Arbeiter in chemischen Fabriken*, p. 37) that a by-pass should be made from the burners directly into the chambers, which should be opened by means of a damper every time a burner is charged, is altogether impracticable, and is evidently not practised anywhere. The difficulty, however, is solved by connecting, during the time the kilns are being charged, the ash-pit (by means of a special flue) with a chimney producing but little draught, so that no burner-gas is drawn downwards into the flue and the chimney, but the burning of pyrites in the kiln is interrupted.

This is done at the Rhenania Chemical Works by means of the arrangements shown in Figs. 98 to 101, which, at the same time, illustrate the form of burners (p. 428) frequently employed on the Continent, where the burners have a common gas-space, the pyrites lies on the grate in rather shallow layers ($19\frac{1}{2}$ in.), and the cinders are removed by means of bogies run underground into the ash-pit. The burner-gas in the ordinary way passes from the dust-chamber through pipe *h* into the Glover tower. Each time the cinders are let down into the ash-pit by shaking the grate-bars, damper *b c d e* (Fig. 100) is shut down, so as to close flue *f* against the outer air, but not hermetically, and damper S is opened, which leads through *g* into a chimney, which is *not* connected with any furnace, and is only 25 or 30 ft. high, so that it just projects over the roof of the shed. The small quantity of air which enters round damper *b c d e* is partly drawn into this chimney, and the pyrites consequently burns so slowly that no gas issues from the doors a, a_1, a_2, a_3. The men now charge the burner with fresh pyrites through these doors, shut the doors, let down damper S, and raise damper *b c d e*, whereupon the evolution of sulphur dioxide recommences, and goes on all the more regularly the more burners are united in the same set. Experience has shown that no sulphur dioxide is drawn down into *f g* during the operation, so that none can escape through the special chimney.

The Stassfurter Chemische Fabrik, vormals Vorster & Gruneberg (Ger. P. 100708), employs a flue connecting two sets of burners, or the single burners of a set, below the level of the grates. In this case, when the charging-doors of one burner are open and those of the other burner are shut, the air-openings below the grate being shut in both, the second burner will draw its supply of air from the first, through its open doors, so that no gas will blow out of these.

Zavelberg (Ger. P. 170602) shifts the pyrites cinders from

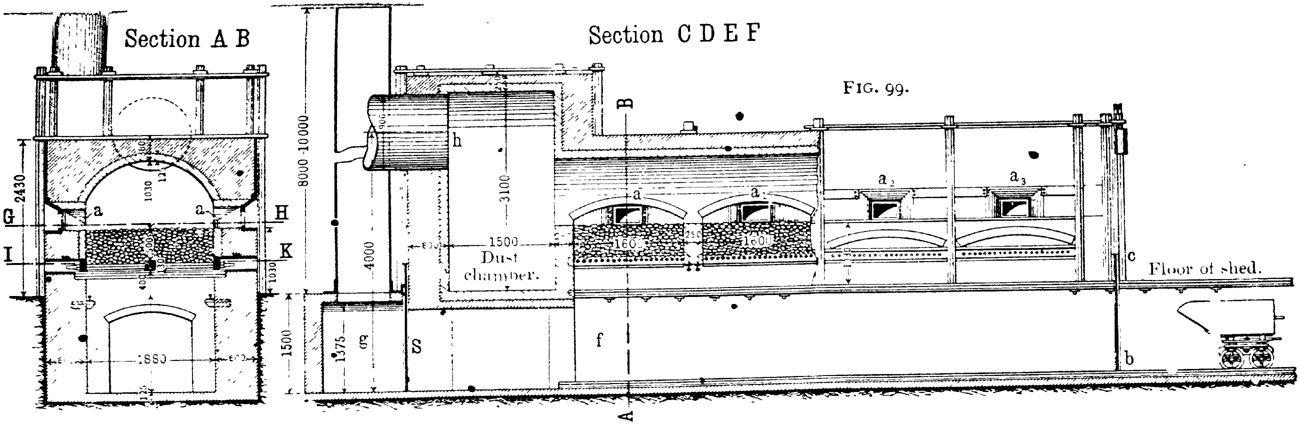

FIG. 99.

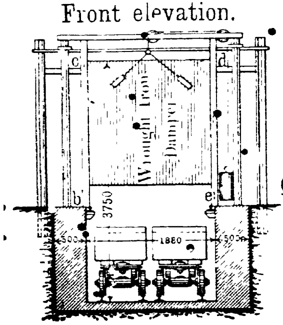

FIG. 100.

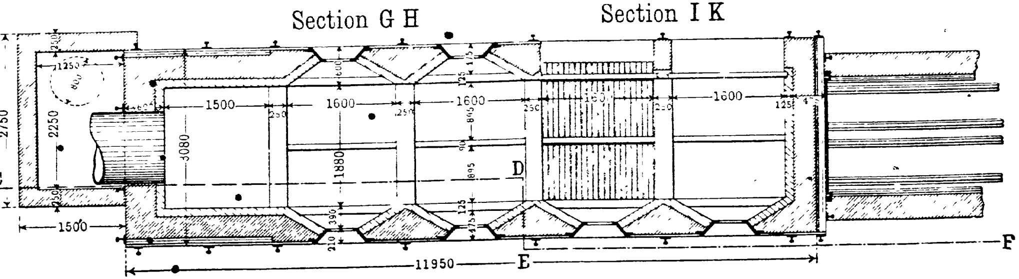

FIG. 101

the burners into air-tight cooling-chambers; the SO_2 is passed back to the burners, and the dust is drawn off by suction.

In properly constructed pyrites-kilns, all *doors* for charging, working, shaking of the bars, and getting out the cinders either run horizontally in grooves, or, still better, they are hung on hinges; and the door-frame, cast upon the front plate, is made to slant forwards below, sometimes also sideways, so that the door lies fast upon it by its own weight. As both the door-frame and the edges of the door touching it are planed, the doors close tight without any luting, whilst those running in grooves must be made tight with lime-putty.

All *brickwork*, so far as it is affected by the heat (that is, the walls above the grates, the arch, and the gas-flue), is lined with fire-bricks; the total thickness in front is one brick, behind (or in case of a partition between two rows of burners) two bricks. The side walls dividing each two burners of a row are 1½ or 2 bricks thick, but they diminish upwards to one brick. The roof need only be 4½ in. thick. The mortar is fire-clay, as usual; in the colder parts, such as vertical gas-shafts, flues, etc., this does not stand so well as boiled-down tar and sand.

F. J. Falding (*Min. Ind.*, vii. p. 666) constructs the first layer behind the cast-iron front plates of hollow bricks, so that air-channels are formed from the grates upwards to the top of the burner. This keeps the burner-room cool and easier to work in, at the same time obtaining heat for concentration in acid pans on the top of the burners, or for increasing the efficiency of the Glover tower, or for supplying the burners themselves with hot air, which is an advantage in some cases.

Zanner (*Z. angew. Chem.*, 1907, pp. 6 *et seq.*) urges the prevention of losses of heat in many parts of the sulphuric acid plant, especially the pyrites-burners, by suitably coating them with bad conductors of heat.

Of course the burners are well bound together, either by special uprights and tension-bars, or by flanges cast to the front plates, provided with holes for the cross-bars (Fig. 87, p. 426).

Opinions as to what *size* the burners are to be made vary a good deal. Frequently smaller burners are met with, about 4 ft. 6 in. to 5 ft. from the outside to the inside of the back wall. The reason given for this is that longer grates cannot be served so well, and that in a larger burner the newly-charged ore forms too shallow a layer (the depth of the whole layer of pyrites, including the partially burnt ore, is not in question here). I have, however, for many years employed larger burners, nearly 6 ft. from the front to the back end of the grate, and have burnt my ore better than the majority of other works using the smaller burners. Certainly, the usual 7-cwt. charge had to be all put in at once, whilst in the smaller burners it is introduced in two halves every twelve hours; and many practical men assert that a twelve-hours' is preferable to a twenty-four hours' charging; but this is not borne out by experience. It is, however, a decided mistake to try burning a much larger charge on the larger grate, say 8 or 9 cwt. This can only be done with poor ores, such as are not in use at the present day, except locally; richer ores, especially those containing copper, are sure to be fluxed by the heat getting too high, and cause the greatest trouble. As a result of long experience, I am inclined to consider a grate-surface of 4 ft. 6 in. by 5 ft. 8 in., and a depth of pyrites of 2 ft. 3 in., very favourable for burning 7 cwt. of 48 per cent. Spanish ore, changing once every twenty-four hours.

The rate of burning just mentioned equals 30 lb. of 48 per cent. pyrites per superficial foot of grate in twenty-four hours. With poorer ore (40 to 42 per cent.) I have certainly burnt in the same grate 8 cwt. (= 35 lb. per square foot), and with 38 or 40 per cent. ore even 9 cwt. (= nearly 40 lb. per square foot). In England the maximum quantity of pyrites burnt per square foot of grate will very rarely exceed 40 lb. of 48 per cent. pyrites; reliable figures from one of the largest works are $35\frac{1}{2}$ and 39 lb. In German works, according to Hasenclever, using Westphalian pyrites, the proportions were 41·6, 44·5, 57·8, 60·3, and 65·0 lb. (Wagner's *Jahresber.*, 1871, p. 212). Bode (*ibid.* 1874, p. 245) quotes for Westphalian pyrites of 41 or 42 per cent. 50·7 to 64·0 lb.; for Norwegian ore of the same strength, 38·3 lb.; for Valais ore, with 35 per cent. sulphur, up to 92 lb. per square foot in twenty-four hours. Favre (*Monit. Scient.*, 1876, p. 271) states as the most favourable ratio in his experience 55·3 lb. of 40 per cent. pyrites per square foot in twenty-four hours.

At the Oker works, in 1901, the roasting area of the three deep kilns (p. 422) serving for a chamber set of 5289 cb.m. amounted to 33·55 superficial metres, that is 0·00634 superficial metre per cubic metre of chambers. The quantity of ore roasted per square metre in twenty-four hours was 0·45 ton copper-ore, 0·50 ton pyritic lead-ore, 1·40 ton copper-matte, 1·60 ton lead-matte (*cf.* p. 115 on the composition of these ores).

In 1902 the Rhenania works at Stolberg considered 200 kg. Westphalian pyrites per superficial metre grate-surface as the normal quantity; with 230 kg. the degree of desulphurisation was somewhat less. The former is = 40 lb., the latter = 46 lb. per superficial foot.

In England a number of years ago many pyrites-burners were made about 33 in. wide and 26 in. from front to back at the fire-bars, but 42 in. square at the level of the bottom of the charging-door, giving a slope of 6 in. back and 9 in. sideways. Later on burners were made larger, say 39 × 42 in. at the bars and 48 × 51 in. at the charging-doors, many going up to 54 in. wide and 60 or 66 in. from front to back at the fire-bars. The smallest sizes burn about 4 cwt. of Spanish ore = 44 lb. per square foot in twenty-four hours; the largest sizes 7 cwt. = 31 lb. and upwards per twenty-four hours. The most usual size is about 16 to 18 sq. ft. at the fire-bars and 22 to 24 sq. ft. at the base of charging-doors, burning 7 cwt. daily = 37 to 41 lb. of ore per square foot. This is about the maximum for rich ores consistent with proper freedom from fluxing, but poor ore may be burned in larger quantity (Thorpe's *Dict. of Applied Chemistry*, iii. p. 719). With the very well-burning Agnas Teñidas ore Davies (*Chem. Engineering*, ii. p. 124) states the proper charge = 2·3 lb. per square foot per hour = 55 lb. per day, in which case the cinders tested 1 per cent. S.

Sets of burners.—It is hardly necessary to say that the pyrites-burners are always built in *sets*. Usually twelve to twenty-four burners are served by the same set of men; and they must be worked so that every one gets its regular turn, as is evident from the necessity of a regular evolution of gas. Frequently the burners are built underneath the acid-chambers. Not only must they in any case be protected by a roof against rain (if not placed underneath the chambers), but they must not stand in a space open at the sides, since strong winds would interfere with the draught, and cause them either to go too fast or to blow out at the doors. It is best to protect them by light walls or by a brattice with shutters adjustable according to the direction of the wind.

As the drawings of the English burners (pp. 425 *et seq.*) show, each burner is independent of the other, and they do not communicate one with another, but only with the common gas-flue. Each burner, then, ought to have its own damper, which is not always the case. On the Continent, frequently the single burners are separated merely by low walls; the ore in this case lies only about 18 or 20 in. deep on the grates, and the whole set is like one large burner with a divided grate (p. 434). It is, of course, in this case not possible, as on the English system, to treat each burner individually, to give it more or less draught, to isolate it for repairs, etc. Nevertheless this system is in favour with some of the more experienced Continental manufacturers, who say that 18 in. depth is quite sufficient for the rich ores, now universally employed, and that the connection of the gas-space of all burners into one whole is preferable to the English system, because one burner can aid another and the whole is visible at a glance. Evidently this system, of which good illustrations are given in Figs. 97 to 100, p. 435, answers its purpose as well as the English; and in a special case, in which I saw a set of English burners working alongside a set of burners of the kind just described, the manager informed me that he preferred the latter, because it was easier to regulate the draught than with the English burners.

In Continental works possessing no Glover tower it is usual to concentrate the chamber-acid up to 144° Tw. in leaden *acid-pans*, which are mounted on the top of the burners, and are heated by their waste heat. Of all plans for concentrating sulphuric acid this is, as we shall see later on, the cheapest, only excepting the Glover tower. There is no reason why such pans should not be placed on the English burners as well; but even before the Glover tower made the use of lead pans superfluous to a great extent, the above arrangement does not seem to have been practised in England, where, however, the space on the furnace-arch is otherwise usefully employed for drying "balls" from pyrites-dust, etc. There are also, as we shall see in Chapter IX, sometimes reasons against placing the pans on the top of the burners.

The "*potting" of the mixture of sodium nitrate and sulphuric acid* (liquid nitric acid is not used in England for this purpose) is now nearly always done in such a way that the burners are not disturbed by it. Formerly the pots were frequently put on pillars between two burners, with a common gas-space; these were provided with special potting-doors in the burner-front, and cast-iron dishes as saucers for receiving the stuff that boiled over; these saucers were inclined towards the doors, so that the nitre-cake could not so easily run into the burners; but it got out of the doors, which made them look very dirty; and ultimately it also got into the burners themselves. None of the better factories have this arrangement now, but all pots belonging to a set of burners are placed in a separate "nitre-oven," which is nothing but an enlargement of the gas-flue, and either situated over the burners or on pillars outside the same. The latter is preferable, for also here there is always a metal saucer provided for catching the boiling-over nitre-cake; this may be cracked before it is noticed, and much nitre-cake may get into the burners, doing great damage. If the arrangement is similar to Fig. 88, p. 427 (where, by the way, the nitre-pots are replaced by a better contrivance to be subsequently described), no risk of the above-mentioned kind is run.

Favre (*Monit. Scient.*, 1876) reports that the works in the south of France use pots of 2 ft. 7½ in. × 1 ft. 6 in. × 12 in., standing on a bridge between two burners; and he also mentions the drawback of boiling over into the burners. This would show that those works, even in 1876, were in a backward state.

Special nitre-ovens are quite unnecessary where the nitric acid is charged through the Glover tower, as we shall see in that chapter. In Chapter V. we also describe special shapes of nitre-ovens.

Special Shapes of Pyrites-burners.

Addie (B. P. 180 of 1886) describes a peculiar pyrites-burner. It consists of a cupola, brought to a white heat, in which the pyrites is charged together with sandstone or other slag-producing material, and is burnt by a hot blast, the cinders being reduced to a molten slag which is run off from time to time. Unless this apparatus was intended for some very special purpose, not apparent at first sight, it must be pronounced as impracticable so far as the chemical manufacturer is concerned.

The methods described in the patent of Hargreaves, Robinson, and Hargreaves (B. P. 5681 of 1886) for treating pyrites are evidently less intended for the manufacture of sulphuric acid than for the recovery of arsenic, antimony, copper, silver, and gold. A whole set of burners is combined in such a way that the air or the gaseous products at first formed can be successively passed through them in regular rotation. The air, previously heated in recuperators, passes downwards, first through nearly exhausted ore, afterwards successively through ore containing more sulphur. The residual ore is treated with acid gases, in order to bring the metals into a soluble state. For details we must refer to the patent specification.

Explosive pyrites (*cf.* pp. 80 and 106) is treated by the United Alkali Co. (B. P. 7915 of 1905) by previously heating for twelve hours on hearths, placed below the gas-flue near to the pyrites-burners, on a higher level, so that the pre-heated ore which has now lost its explosive property can be shifted downwards into the burners.

Burners for Roasting Copper-matte.—Haege (*Berg. u. Hutten. Zeit.*, 1893, p. 383) describes the process introduced by him at Britonferry, near Swansea. The copper-matte produced there could not be roasted in Mansfeld kilns, nor in ordinary pyrites-burners. The desired result was obtained by increasing the heat, in the first instance by a suitable treatment of the matte, and in addition to this by improving the construction of the burners. The matte was rendered porous by tapping it on to a sand-bed slightly moistened and dusted over with fine coal. It was then crushed by a Blake's stone-breaker, in which one of the corrugated faces had been substituted for a smooth one, so that flat more tightly lying pieces were obtained, which were separated from the smalls by a riddle with meshes of ⅜ in. width. The burners were of the ordinary shape of English pyrites-burners, described above, but of slightly different dimensions:—Grate-surface 4 ft. 3 in. by 4 ft. 4 in.; area at the level of the upper working-surface 5 ft by 4 ft. 9 in.; height from grate-bars to the upper working-surface 2 ft., to spring of the arch 3 ft. 4 in., to the crown of the arch 3 ft. 8 in.; smoke-flue at the lowest point 6 in., at the highest 1 ft. 4 in.; total outside height 7 ft. 10 in. The heating-up takes place from the top, exactly as described in the text; the burners are ready for work in two or three days. Each burner then receives a charge of from 6 to 7½ cwt. of crude matte every twelve hours. After three hours everything becomes red-hot, after six hours a bright cherry-red heat is attained. Now the interior of the burner is worked up through the middle door by means of a steel poker, 2½ in. thick, pointed at one end; any lumps formed are broken up; and this working over is continued through the upper door. After another two or four hours the heat is at its maximum; the upper working-door is now mostly at a dark-red heat. Then the heat decreases. Eleven and a half hours after charging the grate-bars are turned and shaken, in order to remove the roasted matte, and after twelve hours a new charge is made. There is no picking out and recharging of imperfectly roasted matte, since everything is well finished. The draught must be well regulated; there should be a slight plus-pressure within the burner. In this way mattes containing from 20 to 47 per cent. copper are treated. The poorer matte yields rather hotter and better gas and more sulphuric acid than the richer. With 20 per cent. matte the roasted product contains 9 per cent. sulphur, with rich matte it contains 11 per cent. sulphur; both are at once ready for the concentrating work. From 40 per cent. matte about 47 or 48 per cent. of the weight of roasted matte is obtained in the shape of chamber-acid of 110° Tw., with consumption of 0·8 to 1·0 nitre per cent. of chamber-acid. The gases are hot enough to thoroughly decompose the mixture of nitre and sulphuric acid in the nitre-oven and to denitrate the acid in the Glover tower; the acid flows from this with a temperature of 140° to 155° C.

Working of the Pyrites-burners for Lumps.

In order to *start a burner* it is first, if newly built, dried by a slow fire in the usual way, and then filled with burnt ore to within 3 in. below the working-door. If no burnt ore can be procured, ordinary road-metal, etc., may be taken, broken sufficiently to pass between the grate-bars when they are turned. The draught-hole of each burner is closed by a damper, and the working-door is left open. Then ordinary fuel (wood or rough coals) is heaped on the ore and lighted. After twelve or twenty-four hours the burner and the uppermost layer of the ore will have reached a dull red heat; the rougher parts of the fuel still present are then drawn out and an ordinary charge of green pyrites is put on. By the heat of the burner walls, that of the ore below, and the fuel still present, the fresh ore will soon be lighted; when it is fully burning, the working-door is closed, the damper closing the access to the gas-flue is opened, and the gas allowed to go to the acid-chambers. Care must be taken in lighting up not to go too far, which would damage the burners.

Thus the process is started; and it is now continued regularly and uninterruptedly till it has to be stopped for external reasons. Repairs are very rarely necessary in pyrites-kilns; but those of other parts of the acid-making apparatus may compel their stoppage. At some English works the dampers are put in every Saturday at midnight, and are opened only on Sunday at midnight; in the meantime, all other openings are well closed; and the burner thus keeps its heat so well that the new charges at once take fire when brought in. If any temporary interruption of work does not last beyond four or six days, usually the burners can be kept hot enough in this way to be started without any fresh lighting-up by means of fuel.

The regular burning-process has a double object, from which follow all the precautions to be observed. In the first place, the sulphur contained in the ore is to be burnt as far as possible; and, secondly, a just sufficient quantity of air is to be employed, no more and no less than is required for the chamber-process. This means, besides the air necessary for burning the sulphur to sulphur dioxide, introducing as much more *air* as is required for oxidising the latter to sulphuric acid, and, moreover, a certain excess of air found necessary in practical work. Anyhow, therefore, the air will be more than just sufficient for burning *all* the sulphur contained in the pyrites; and the second condition seems thus to imply the first. But this can be said only for brimstone and for pure pyrites not containing any zinc-blende or galena, etc.; for only the former can be desulphurised completely by their own heat of combustion.

The sulphates of iron, which are always partly formed as intermediate products, are decomposed again at a comparatively low temperature into Fe_2O_3, O, and SO_2, or into Fe_2O_3 and SO_3, for which the heat of the burners is quite sufficient. This reaction does not go on quite so easily in the case of the sulphides of copper; but the temperature of decomposition of $CuSO_4$ is also within a red heat. Moreover the copper-extraction works do not want all the sulphur to be burnt, but allow a residue of from four to at most six per cent. sulphur in the cinders. If, however, the ores contain blende or galena, which on burning are transformed into zinc and lead sulphates, the burner cannot possibly effect a total desulphurisation; for these sulphates are only decomposed at a strong white heat, which is not allowable in a pyrites-burner, and they must thus remain as such in the cinders. Furthermore, if the pyrites contains calcium sulphate or carbonate, a corresponding quantity of $CaSO_4$ will remain in the residue. Any barium sulphate present would not be taken notice of in the testing of the pyrites or the cinders, being classed among the "insoluble."

In the case of the usual descriptions of pyrites, not containing any considerable quantity of zinc or lead, the burning of ore in lumps will reduce the sulphur in the cinders with good work to 3 or 4 per cent. Less than 3 per cent. of sulphur rarely occurs on an average of the whole year; but with very good ores it may go down to 2½ per cent. At the Rhenania works, at Stolberg, even pyrites with 6 or 7 per cent. Zn is burnt down to 2 or 3 per cent. S, exceptionally 4 per cent. (information received in 1902). Most frequently the limit stated above for good work is exceeded; some works leave 6 or 8 per cent. of sulphur, and even more, in their cinders, whilst their neighbours only leave 4 or 5 per cent. in the same ore. The fault of this may be due either to the description of burner employed or to the style of work. If, by the construction of the burner, the pyrites forms too shallow a layer, and this is let down too soon on shaking the bars, it will easily come out badly burnt. But even if the burner is correctly built, much still depends upon the skill and care of the burner-men.

Excellent results are obtained with some of the very rich descriptions of Spanish non-cupreous pyrites which have for some time past come into the market (p. 81). These pyrites can be burnt down to 0·5 per cent. of sulphur in the cinders, so that the latter can be sent straight to the blast-furnaces. But if this degree of purity is to be obtained, the place in front of the kilns, where the burnt ore is drawn out, must be kept perfectly clean, so that no green ore can get mixed with the cinders; and any portions of these which have been spilt from the discharging bogies on to the ground must not be shovelled back into them, as they will have some admixture of dust from green ore, but they must be put back into the kilns.

How much depends upon employing the ore in *neither too large nor too small pieces*, and upon keeping the pieces of as *uniform a size* as possible, has been mentioned on p. 416. Only then will it be possible to regulate both the depth of layer and the draught in a satisfactory way.

Whether pyrites is properly burnt or not can be recognised to a great extent by the eye. By the burning-process the pieces swell out and burst; they become light and porous, and assume the red colour of ferric oxide, in the case of cupreous pyrites a more blackish-red colour. The burnt ore ought therefore to consist of light porous pieces of the proper colour, apart from the powder always present in large quantity, which is generally sufficiently burnt off. Already, on taking up the larger pieces, their weight will allow a rough judgment of the state of the burning; and this can be more distinctly recognised by breaking the pieces and observing whether they contain a raw core in the centre. Also the presence of many slags (scars) on the cinder-heap is a proof of bad burning.

Important as these empirical signs are, no well-managed factory will be satisfied with them, but will from time to time, daily or at least twice a week, have the cinders tested, after having drawn a large sample and reduced it properly. At all events the above-mentioned empirical signs have hardly any value for small ore.

The chemical testing of pyrites cinders (*burnt ore*) can take place by exactly the same methods as described in Chapter II. for the analysis of pyrites itself. It is there shown that in the case of burnt ore more expeditious methods may be used, and that among these that of Watson-Lunge (igniting with sodium bicarbonate and titrating the undestroyed sodium carbonate) seems to be the most accurate (p. 104).

The *sulphur* contained in the burnt ore is no longer in the shape of FeS_2, apart from any quite raw cores in large pieces. But even fine or quite porous cinders, burnt as well as possible, also those from pure pyrites free from lead, zinc, and lime, always contain sulphur; and as this cannot be present in the shape of FeS_2, the question can only be whether the cinders contain FeS or sulphates of iron (most probably basic ferric sulphates), or both. According to Scheurer-Kestner and Rosenstiehl (*Bull. Soc. Chim.*, 1868, ix. p. 43), the cinders contain essentially FeS; they give two analyses—(i.) of properly burnt ore; (ii.) of an operation carried on too hot, so that the ore had fluxed. Both are from Sain-Bel pyrites, containing 46·1 per cent. sulphur in the pieces and 49·28 in the smalls.

		I.		II.
Moisture		1·0		
FeS		8·5		27·2
Fe	5·4		17·3	
S	3·1		9·9	
Oxide of iron		72·0		62·4[1]
Fe	50·4		41·0	
O	21·6		21·4	
Quartz		18·5		10·4
		100·0		100·0

From these analyses it would appear that there was no ferric sulphate whatever in the residues, which is, however, very improbable, as sulphate can be always found by washing with water (*cf.* Bode, *Dingl. polyt. J.*, ccxviii. p. 327, and a number of analyses quoted in the chapter treating of the recovery of copper from the cinders).

According to Troost, the first reaction in the burners is $3FeS_2 = 2S + Fe_3S_4$. Regnault holds that the sulphide formed has the formula Fe_5S_6. Lemoine (*Fischer's Jahresber.*, 1899, p. 355), from observations made in a Malétra shelf-burner (see *infrà*), believes that in the upper layers there is always a distillation of sulphur, which afterwards burns with a blue flame. Lower down this is no longer the case, either because here most of the pyrites is already reduced to FeS, or because the temperature is too low and the supply of oxygen too great for the formation of free S. Ferric oxide appears only after roasting for two and a half hours. The action on pyrites seems to commence from the outside, where there is combustion into Fe_2O_3, and the action of the heat thereby produced on the inner part brings about a decomposition into FeS and S. The S distils and burns outside, the FeS is oxidised by the Fe_2O_3, which is again reformed by the outer air.

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[1] The calculation does not agree here; 62·4 Fe_2O_3 would contain 43·68 Fe.

Richters (*Dingl. polyt. J.*, cxcix. p. 292) quotes the following analysis of burnt ore from the Silesia works at Saarau:—

Water	4·35
Iron	43·36
Manganese	0·16
Silica	13·92
Alumina	4·84
Lime	0·02
Zinc oxide	8·83
Sulphur trioxide	4·35
Sulphur	1·53
Oxygen and loss	18·64
Nickel and arsenic	traces
	100·00

Phipson gives the following analysis of residue from Irish pyrites (*Chem. News*, vol. xviii. p. 29):—

Zinc oxide	5·50
Cupric oxide	2·86
Manganese oxide	1·60
Nickel and cobalt oxide	0·12
Cadmium oxide	0·01
Lead oxide	1·67
Antimony oxide	0·04
Ferrous oxide	1·17
Alumina	3·25
Sulphur	2·60
Thallium	traces
Indium	traces
Gangue	15·00
Ferric oxide	65·99
Lime	0·11
Magnesia	0·08
	100·00

All that has been said (*cf.* p. 445) respecting the maximum of sulphur in the cinders to be aimed at, only refers to the burning of pyrites proper—that is to say, of ores containing essentially FeS_2, and employed exclusively as a raw material for vitriol-making, in which case the cinders are as good as worthless. Just in the same line are those *cupreous pyrites* (with less than 4 per cent. of copper) whose copper can only be extracted by the wet process; for these the above-mentioned rules for the sulphur in the cinders are equally valid. But the case is quite different with a number of ores where the residue from the burning is regarded as by far the most important product, and where the gas is only a by-product, often only converted into sulphuric acid in order to get rid of it. To this category belong blende, copper-pyrites, coarse metal, etc. Here the burning-down to the above-mentioned minimum of sulphur is partly not possible, partly not even desirable (as for copper-pyrites); and there exist for each case definite rules, which, however, do not belong to the domain of acid-making, but to that of metallurgy. Even where a larger percentage of sulphur is required for further metallurgical operations, it is more rational, so far as concerns the acid-maker, in order to save labour, burner-space, etc., to burn the material as well as possible, and to supply the necessary sulphur afterwards by adding a little green ore; thus, for instance, the copper-extraction works proceed when they receive the cinders too far desulphurised. The case of zinc-blende is a special one and will be dealt with later on.

We now pass on to the second fundamental condition of proper work in the pyrites-burners, viz., *that neither too little nor too much air be employed.* At this stage we leave out of consideration the absolute quantity of air required, and only treat of the practical rules and of the appearances observed in the burners themselves. If too little air is admitted, whether because too few holes in the bottom door have been opened, or the damper in the draught-hole has not been enough drawn, or because the pipes are stopped up with dust, or the draught in the whole chamber system is insufficient from one cause or another, the same thing will happen as in the case of sulphur-burners when they get too hot: *sulphur* will *sublime* as such, and will be deposited in the flues, the dust-chambers, the Glover tower, or the chambers themselves. It is, however, a more frequent and serious consequence that, in the case of insufficient draught, the often-mentioned *slags* or *scars* are formed. These, as Scheurer-Kestner and Rosenstiehl have shown (*loc. cit.*), consist mostly of *iron monosulphide*, FeS, which is necessarily formed when FeS_2 is heated, with exclusion or insufficient supply of air, together with free sulphur. It is easily fusible, and fluxes in the burners to more or less large cakes or scars, upon which the air has practically no action. The FeS fluxes all the more easily, as in the case of insufficient supply of air, where no cooling by the excess of air takes place, more heat is developed in certain places than when the supply of air is abundant. The scars mostly enclose some green pyrites, and in this way cause a further loss of sulphur. A much greater loss is occasioned by their stopping the passage of air, so that the ore above and below a scar is very incompletely burnt. The heat is locally increased and driven further down than it ought to be; the zone of combustion is removed further downwards; and on letting down the ore the pyrites partly comes out incompletely burnt. If scars have formed in the burner, they naturally descend as the cinders are let down, and they would ultimately lie immediately on the grates and entirely stop them up. This, however, must be prevented by all means. A careful workman always breaks up the surface of the old ore before putting in a fresh charge; and thus he finds out whether any scars have formed, which mostly takes place near the surface: they can then be easily brought to the surface by means of hooks and pulled out at the door. But if they had been overlooked at first and have got lower down, in doing which, they constantly increase in size, their removal is more difficult. Then a very large and heavy *poker* of the best tough iron (these are made up to 12 ft. long and 2 in. thick), bent in the way shown in Fig. 102, is introduced into the burner through the charging-hole, and the men work it till they have got the point *a*

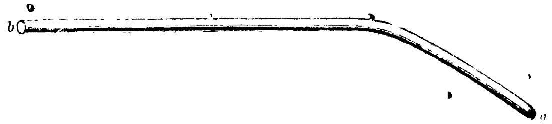

FIG. 102.

underneath the scar. Several men, working at the end *b*, then try to lift up the scar, in spite of the resistance of the superjacent mass of pyrites. This labour is very disagreeable, exhausting, and difficult. The middle doors, between the charging-door and the grate, found in all pyrites-burners, are only used in extreme cases.

In the low burners mentioned on pp. 428 and 434, where the ore lies only at a depth of 20 in., scarring is next to unknown, at least if the ore is very carefully sized, so that all passing through a ½-in. riddle is kept out. This agrees with the facts which will now be explained.

Apart from other causes, the supply of air in a burner may be insufficient because the ore lies too deep. As the depth of the ore depends upon the vertical distance between the grate and the working-door, it follows that for ores behaving very differently in this respect differently built burners must be used. Thus the deep burners built for Irish pyrites had at once to be given up when Spanish pyrites began to be used. With the same height of pyrites which was just right for the poor ore, in order to keep the heat better together, the rich cupreous ore, in itself more fusible, became far too hot, and, moreover, the air could not pass through quickly enough to make a *complete* burning of the ore possible at every point; from both causes combined followed this effect (easily comprehensible after what has just been said), that the scarring became excessive. It is always much more feasible to burn poor ore in a shallow than rich ore in a deep burner.

Insufficiency of draught, if very considerable, will be easily recognised by the gas blowing out of all the joints of the burners, and especially coming out in force whenever the working-doors or the bottom door are opened. On the other hand, the draught should not be so strong that too much air will get into the chambers; the gas ought to be kept as rich as possible, as will be shown hereafter. It may be assumed that the draught is just right, if, on opening the small slide in the working-door, neither gas nor flame issues from it, nor, on the other hand, the flames inside the burner perceptibly tend towards the draught-hole. They ought to rise up perpendicularly and quite steadily; and on opening the door they may even tend slightly towards it. As, however, the exact regulation of the draught can only be effected by regulating the holes in the bottom door, and as on each opening of the doors above or below the grate much more air must get in than is necessary, of course the periods during which the doors are opened should be restricted as much as possible, and the charging, shaking of the grates, and discharging managed as quickly as possible. It is very advisable to close the holes in the bottom door completely while the top door is open, or to proceed in the way described on pp. 433 *et seq.* If the draught is not very copious, whenever the door is opened, there will be no room for so much air rushing in, in consequence of which a portion of the gas will rush out and get into the burner-house; this is both a loss and a nuisance to the workmen, and, in case of greater quantity, also to the neighbours.

For regulating the supply of air several plans are possible. The regulation takes place either *before* the grate, by the holes in the bottom door, or *behind* the grate, by means of the damper in the draught-hole or that in the large chimney behind the chambers, or else by fan-blasts (*cf.* Chapter V.). Regulation behind the burners is only available where all the burners have a common gas-space; otherwise the draught through the chimney or fan must be equal to the maximum amount required for all the burners, and must be changed according to the atmospheric conditions, each burner being regulated separately. This would be done best and most safely by the dampers in the draught-holes connecting each burner with the gas-flue; but these are rarely used for this purpose; they would have to be made very tight-fitting, and then would easily get fast by flue-dust. Therefore here also the draught is made sufficient for all eventualities. The real regulation of the air, at least generally in England, takes place by means of the holes in the ash-pit door, of which a sufficient number are closed by plugs or otherwise. Scheurer-Kestner went so far as to regulate the supply of air by means of a Combes' anemometer; but this can only have been done for isolated experiments, since such a delicate instrument can hardly have been kept fit for use for any length of time in an atmosphere thus exposed to acid vapours and to dust. It is therefore left to the burner-men to open or close the holes in the door as required. At the Rhenania works (1902) they regulate the supply of air, apart from the exit damper, merely by a slide damper, shutting off the flue below the grates in which the cinder-bogies are placed.

The supply of air is usually regulated by the following practical rules:—At the beginning (that is, immediately after making a fresh charge) the burner does not require very much air, till the ore has caught fire, which will take half an hour or an hour. Then more air must be admitted, always with the above-mentioned restriction: that the flames rise perpendicularly, and tend slightly towards the slide when this is opened. When, however, the principal portion of the sulphur is burnt and the flames become scarce, the air is altogether shut off, and further action is left to the heat of the burner. About two hours before it is time for recharging, the working-door is opened and the ore is well raked and turned over by means of a hook to a depth of 3 or 4 in., and any small scars are removed. If now blue flames appear to any extent, this proves the burning not to have been sufficient, and a little air must be admitted. When the whole time is up, be it a twelve hours' or a twenty-four hours' turn, the air is entirely shut off at the bottom, the small doors covering the grate-bars are opened, and the latter are turned two or three times, leaving each alternate one out. During this the workman must look through the working-door, to see whether the layer of ore is let down evenly all over; he can easily manage, determined by the eye, not to let the ore down too much or too little. Then, as quickly as possible, the new charge of ore in pieces (usually with a little dust), which must have been lying ready in front of the burner, is put in, and the process begins again. It is evident that there must be a regular rotation, so that a fresh burner comes in turn every hour or so; this is both indispensable for a regular evolution of gas, and convenient for distributing the labour over the day.

The burner-men ought to shake the grates quite evenly for the purpose of discharging, so that the ore does not come down more quickly in one place than in another, and to take care that only cold, thoroughly exhausted cinders, but no red-hot ore, comes down. They ought then to work up the ore on the top through the doorway with their pokers, and rake the surface so as to make it even again. Then they must charge the new ore equally all over, starting about 2 in. towards the door from the back and the sides. Two men can attend to a set of eighteen or twenty burners, consuming from 6 to 8 cwt. of pyrites each every twenty-four hours, including the wheeling away of the cinders and the potting.

The interior of a burner, after the throwing-in of a fresh charge, is, of course, at first quite black. Gradually small blue flames appear, which become larger and more lively and cover the whole mass. After a few hours they become scarcer again; but the mass in the meantime has become red-hot. Later on it cools again; and towards the end of the period there is no glowing visible at the surface; but as soon as the mass is stirred up the glowing appears again.

The men like to employ a practical test, to convince themselves that the burner is not too hot for recharging, in the shape of strokes made with brimstone on the burner-door: so long as these take fire at once, the burner is still too hot; only when they remain is it cold enough for charging. Frequently it is necessary to wait a short time, even for a few hours, after shaking the grate-bars and letting down the burnt ore, in order that the burner may cool down a little before recharging it; this has the advantage that the top layer, by turning it over, is caused to burn its sulphur more thoroughly than it can be burnt after cold pyrites has been thrown in.

Generally it takes some time before the men get used to a new kind of burner or of pyrites. If even skilled men are taken from other places, they require special supervision, and still more if a new kind of pyrites has to be tried. If at all possible, different kinds of ore ought not to be tried mixed up, but one kind adhered to for some time, because only in this way do the men get used to a thoroughly proper treatment of the burner. Each kind of pyrites requires a little different treatment as to supply of air, breaking up, etc.

An extremely great help in regulating the burning-process is the *analysis of the gas*, which, however, is nearly always made for a whole set of burners together in their common flue. We shall enter into the details of this later on.

If a pyrites-burner is working properly, it will, if touched outside, be so hot in its upper part (say 6 in. below the working-door) that the hand cannot be borne upon it; farther down it must be cooler; and immediately above the grates it ought to be cold, or at most hand-warm. *This is one of the most important practical signs of the proper working of the burner.* If a burner is too hot below, this may be due to insufficient draught, or (which in the end comes to the same thing) there has either been too much pyrites charged, or there is too much dust in the burner, which has stopped up the interstices. Too much dust may come from bad riddling, from too much having been added on purpose, from the falling of the "balls" inside the burners, or from the decrepitation of "explosive" ores (*cf.* pp. 80 and 106).

In any case, the first thing to be done, apart from removing the cause of the evil, is to again *cool* the excessively hot burner. Above all, *more air* must be admitted; and, in order to drive up the heat more certainly, the new charge must be kept back a little, and no fresh ore put in the middle, but only along the sides and the back of the burner. It always takes one or two days, sometimes longer, before a burner has recovered its normal temperature. In specially obstinate cases there is nothing for it but making very small charges for a day or two, till matters have come right again. Some prefer taking out the ignited top layer, allowing it to cool a little, and putting it back into the burner, which in the meantime has received more draught, owing to the lower depth of ore, and thus has become cooled.

If a kiln is allowed to go too hot for any length of time, whatever may be the cause (want of air, too large charges, stopping up by dust, bad breaking up), the consequence will always be the same, viz., increased *scarring*, with all its unpleasant accompaniments. I have had to deal with cases where the scars became so abundant that the burner had to be put out, the grates had to be drawn, the whole of the stone taken out, and the burner freshly filled up.

Of course it also sometimes happens that a burner goes *too cold* and the fresh charges take fire too slowly. This may be caused either by insufficient draught or by too small charges, and can be easily remedied in either case. If it has, however, got so far that the new pyrites will not take fire at all, nothing remains but to put in very hot ore from some of the other working-burners; in this way the matter may always be put right with some patience, unless large scars are lying on the grates, or there are other serious faults, which must be removed before the burner can be expected to work properly. A frequently employed, but objectionable, remedy against cold burners is to put live coals on the pyrites. The carbon dioxide produced thereby is a great enemy to the chamber process, probably not so much by diluting the gas (for its injurious action is far too great to be attributed to that alone), as by remaining in the lower part of the chambers and preventing contact between the chamber-gas and the bottom acid, till it is removed by diffusion. This point, however, is not yet cleared up.

A pyrites-burner may also go too cold if there is *too much draught*—if, therefore, besides the air required for its intense working there is an excess, which only acts as inert cooling gas. This is a very great fault; for in this case the consumption of nitre is increased and the yield of sulphuric acid very much diminished. Long before the burners cool from this cause, an excess of air may become injurious in this way; and by observing the flames in the burners (much better, however, by the analysis of the gas), it must be ascertained whether the proper proportion of air is present or not.

Balard reports (*Rapports du Jury International*, 1867, vol. vii. p. 29) that in the first trials of Perret and Olivier for employing pyrites in manufacturing sulphuric acid, they at last succeeded in properly conducting the combustion, but obtained a very small yield of acid. They ascribed this to insufficient draught, and applied a fan-blast; but the yield instantly became minimal. Now the other extreme was tried—the air-channels were stopped up with boards covered with sheep-skins and fastened by stays. At once the chamber process became regular, and the key to employing pyrites in the manufacture of sulphuric acid was found. Probably the previous endeavours of Clément-Desormes in this respect were frustrated by his allowing too much air to enter.

Objection has been made by some to the employment of *damp* pyrites (Kerl-Stohmann's *Chemie*, 3rd ed., vi. p. 197), because in this case, on burning, more sulphates are formed, which give off sulphur trioxide; this takes up moisture, and condenses as sulphuric acid before getting into the chambers, destroying the flues and so forth. Even with dry ore in damp weather similar phenomena are said to be observed, and a smaller yield is alleged to be the consequence of the moisture in the air. On my own part, I have never noticed such an effect of damp weather, nor have I been able to learn anything about it elsewhere, in spite of numerous inquiries. It is very desirable that this point should be specially examined. The formation of sulphur trioxide, as well as the occurrence of liquid sulphuric acid, in the connecting-tubes has certainly been established; but it has not yet been proved that the moisture of the air acts so as to increase that formation, and the contrary is more than likely to promote the formation of sulphur trioxide.

People who have no practical acquaintance with the matter, looking at these numerous sources of mishaps, may be inclined to think that the working of a set of pyrites-burners is a most difficult task. But it is far from that. If once the burners are in order, they remain very long so if the burner-men know and perform their duty to any considerable extent, and if proper supervision is exercised over them; the pyrites-burners then give even less trouble than sulphur-burners. Certainly, when they do get wrong, it takes energetic and experienced management to put them right again.

It will now hardly be necessary to explain in detail why there are only narrow limits for each given burner and style of charging, within which the *quantity* of pyrites charged may vary (*cf.* pp. 437 and 438). If too much is charged, the burner scars; if too little is taken, it gets cold. When, therefore, for any reason the daily quantity of pyrites has to be cut down, it is necessary to put out a corresponding number of kilns and to fully work the remainder. Only in the case of brief temporary interruptions is it possible to charge rather less than usual for a few days; but I would recommend even in this case rather to allow the bulk of the burners to go on as usual, and to keep the necessary number hot without fresh charges by closing all openings. Then these kilns will be much more easily put in order by the assistance of the other burners in full work than if they had *all* cooled down.

Employment of Brimstone together with Pyrites.—Westergren (Swed. P. 31999; *Chem. Zeit. Rep.*, 1912, p. 170) prepares SO_2 for the manufacture of sulphide pulp by roasting pyrites with an excess of air, and passing the gases produced through flues in which brimstone is burned, if necessary with admission of more air.

3. BURNING PYRITES-SMALLS.

We have seen above (p. 415) that the fine powder which passes, say, through a ½-in. or at most a ¼-in. riddle must be kept out of the ore going into the ordinary pyrites-kilns. The "smalls," "fines," or "dust" produced in this way, whether it be on breaking the ore at the works or already at the mine, must be dealt with separately.

This can be done in very different ways, according to circumstances. Where pyrites-smalls are not bought as such, the question is only about the dust arriving along with the bulk of the ore, and also that made in breaking. Much more dust is produced when breaking by machine than by hand—viz., up to 20 per cent. in the case of middling hard ores, and even more in that of soft ores. Formerly, before rational and really satisfactory contrivances for the burning of smalls were known, some large factories, which had already mounted stone-breaking machines, went back to hand-breaking, in spite of its costing three to six times as much, merely in order to avoid the excess of dust. This was especially the case in factories using soft ores, such as the Tharsis ore; with Norwegian ores the advantage was always on the side of the mechanical breaking, because these are much harder and make less dust. If the quantity of dust going through the smaller riddle does not exceed 1½ cwt. to the ton, it can be got rid of, according to my own experience, without any special contrivance, in the following way;—The dust is sifted off as usual, and a certain quantity of it is laid down for each burner alongside the pieces. If, for instance, the whole charge is 7 cwt., 6½ cwt. of pieces are used and ½ cwt. of dust; if more dust than this is used, the burner easily gets out of order. First the coarse ore is charged as usual; and then the man throws the dust with his spade along the *sides* and the *back* of the burner, leaving the whole central part free. Anyhow, the ore ought to be levelled with a hook, after throwing in the charge, in such a way as to make it lie higher along the sides and back than in the centre of the burner. The reason is this: the air entering from below meets with much less resistance at the comparatively smooth walls than in the centre of the layer of ore, and it will preferably rise along the former; the centre thus will get less air than the parts next to the walls. If, however, the ore is lying near the walls at a higher level, and especially if the passage of air is obstructed by the dust lying at those places, the draught will be more nearly equalised, and the burning will take place evenly all over the area of the burner. Of course it will not do to proceed too far in this way; nor can it be expected that the result is as good as when lumps and smalls are each treated in the best way suited for them.

Dust made into Balls.

The arrangement just described does not answer if more than 1½ cwt. of smalls to the ton of pyrites has to be dealt with; and special arrangements must then be resorted to. Probably the oldest method, now almost obsolete, is the following:—The small ore is, without further grinding, mixed with sufficient clay to make it plastic, made into a puddle with water, formed into *balls*, and dried on a steam-boiler or pyrites-burner. Rarely less than ten per cent. of clay will be required for this, often more, up to 25 per cent. The balls are then charged together with lumps into the ordinary burners, but never too many at a time (at most one-sixth part of the whole charge), because they fall to powder in the burner after a time, and if used in a greater proportion would stop the draught. Only here and there is such rich clay found that the balls stand pretty well in the burners and can be well burnt off. The workmen dislike them very much, because they disturb the working of the burners, even when the above-mentioned restriction of their quantity is observed; if a burner is not quite warm, they must at once be left off. Some factories, in order to get rid of them without disturbing the burners, burn them by themselves, mixed with "coal brasses" (p. 65)—that is, the pyrites picked out of coals, which always retains some of the latter, and therefore burns more vividly and gives out more heat than pure pyrites; but then it sends the injurious carbon dioxide to the chambers. Usually not much is gained by making the balls with clay, since they so quickly fall to pieces in the burner; and nearly as much can be done by throwing the dust at once into the burner and saving the cost of making the balls. Only by a very strong admixture of clay can the disintegration of the balls be prevented; but then the loss of sulphur and the contamination of the burnt ore is all the greater. In both cases the sulphur left in the burnt ore rises very much, from 6 to 8 per cent. and more. Where the cinders go to copper-extraction works, the use of clay for balls is quite inadmissible.

Wurtz (Amer. P. 252287) mixes the pyrites fines with pulverised metallic iron, moistens the mixture with a solution of ferrous sulphate, and allows the whole to be made coherent by the rusting of the iron.

Wiess (Ger. P. 185602) treats the balls made of pyrites-smalls with coking substances and lime, etc., with a solution of waterglass, in order to increase their cohesion by the formation of silicates.

Robeson (B. P. 1639 of 1908; Ger. P. 238119; Fr. P. 386695) makes briquettes from pyrites-smalls by means of spent sulphite liquor from the manufacture of paper pulp as binding agent. The liquor is first neutralised by caustic soda or lime, and concentrated *in vacuo* to 30° B. The briquettes obtained are hard and not hygroscopic, and the organic matter, introduced with the sulphite, aids in the combustion [but emits injurious carbon dioxide].

Utley Wedge (Amer. Ps. 804690, 804691, 804785, all of November 1905; Ger. P. 181516) employs, as binding agent for pyrites-smalls, ferrous sulphate, by itself or mixed with sodium sulphate and nitrate, and subjects the mixture to heat, insufficient to expel the S from the pyrites, but sufficient to bind the mass.

Ricketts and King (Amer. P. 894799) mix the pyrites fines with a fusible sulphide or other sulphur compound, and subject the mixture, under reducing conditions, to sufficient heat to liquefy the sulphur compounds. The now coherent mass is compressed into any desired shape.

Burning Pyrites-smalls without making them into Balls.

The making up of pyrites into balls with clay is connected with so many drawbacks that something else was soon looked for. This was found indispensable where nothing but pyrites-smalls could be obtained, or where these could be procured so cheaply that acid-makers wished to dispense entirely or partially with using lump ore. At the pyrites-mines there were formerly enormous heaps of smalls, which were not saleable at all and would sometimes have been given away for nothing, just to make room. In other places pyrites only occurs in a loose, roughly crystalline shape; and, again, in others it is obtained by wet preparation altogether in the state of smalls. Thus there was great encouragement for constructing apparatus for burning small pyrites in large quantities.

The contrivances for burning pyrites-smalls may be divided into three classes, namely, those working by external heat, those utilising the heat of ordinary burners for pyrites in lumps, and those arranged for burning the smalls by themselves without any extraneous apparatus.

(a) *Burning Pyrites-smalls in Coal-fired Furnaces.*

Apart from the use of "balls," the oldest plan of dealing with pyrites-smalls is that of spreading them on the bed of a furnace, heated by flues underneath, the fireplace being arranged at one end and the pyrites-dust being introduced at the other, and being gradually moved forward towards the fire end, as room is made for it by drawing out the burnt ore. Since the ore is thus turned over many times on its way from one end of the furnace to the other, the sulphur was supposed to be thoroughly burnt. This is, however, but imperfectly the case, even if the furnaces are made 100 ft. long. Moreover, the cost of fuel in the best case is very heavy (at least 10 cwt. of coal is consumed for a ton of pyrites, usually much more), so is the cost of labour; the continuous opening of the working-doors causes very much false air to get into the chambers, even fire-gases sometimes leak through the furnace-bottom, and therefore the consumption of nitre and the yield of acid are very bad. We shall, consequently, not go into any details respecting these "muffle-furnaces," but refer to the first edition of this work, where, on pp. 186 to 190, the Belgian furnaces, and those of Spence, of Godin, of Imeary and Richardson, are described and partly illustrated by diagrams. Since it has been recognised that no extraneous heat is necessary for burning pyrites-smalls, such furnaces must be looked upon as altogether irrational, and they are practically obsolete now. This, of course, has nothing to do with the fact that similar furnaces are in use for roasting galena and other ores which do require external heat for the purpose.

(b) *Burning Pyrites-dust by the Heat of Burners for Lumps.*

This was considered a great improvement upon the older methods, but it must be equally pronounced obsolete now, at all events in the case of ordinary pyrites. We shall therefore treat these processes very briefly, referring for details to the first edition of this work.

The first furnace for burning pyrites-smalls by means of the heat from lump-burners seems to have been that patented in France by Usiglio and Dony, 24th January 1852, which, however, did very imperfect work. Much more important is the furnace constructed by Olivier and Perret, which was introduced into the majority of French works and was in use there for many years, until replaced by the Malétra burner (*vide* p. 465). Olivier and Perret placed above an ordinary lump-burner a number of shelves made of fire-clay, and charged with a thin layer (not above $\frac{3}{4}$ in.) of pyrites-dust (for exact description and diagrams, *vide* first edition of this work, pp. 193-196). In this way it is possible to burn about 1 cwt. of dust to each 2 cwt. of lumps, the sulphur in the cinders being reduced down to 4 or 5 per cent. The whole furnace was originally about 20 ft. high, which necessitated a second working-stage above the ground. There is, of course, a good deal of labour connected with this system. Later on it was made lower, and so arranged that all the doors were on one side, so that a number of furnaces could be grouped into a set.

In a simpler form, namely, that of a single cast-iron plate, above ordinary lump-burners, this system was introduced into some Tyneside works, first by MacCulloch, but was soon abandoned again (*cf.* first edition, pp. 191-193).

Another way of carrying out the same principle was the furnace of Hasenclever and Helbig (our first edition, pp. 196-201). Here, at the end of a set of lump-burners, a tower-like apparatus was arranged with eight inclined shelves of fire-clay, over which the dust was gradually to slide down and to be burnt on its way. Thus from 10 to 16 cwt. of smalls were to be burnt for each 48 cwt. of lumps; but the principle of automatic sliding-down did not answer; the motion of the dust had to be aided by hand work, with much introduction of false air; and although a large number of these furnaces were erected, principally in Germany, they have been almost or entirely abandoned for some time past, and we abstain from describing them in this edition.

(c) *Burning Pyrite-smalls without External Heat.*

We must, in the first place, mention a plan which does without any special dust-burners, and only represents an improvement in making "balls." It is based upon the fact that pyrites, if it is in the shape of very fine powder mixed with water, coheres to a solid mass *without the aid of any plastic substance.* The fine pyrites-dust, in the presence of water and air, begins to oxidise very soon, even at the ordinary temperature; thus basic ferric sulphate is formed, which firmly cements together the separate grains of dust. This only takes place to a sufficient extent if the grains of dust are very fine and the mixture with water very perfect; and it can never be attained by merely sifting and moistening the fine ore. The ore must therefore be ground finely with water in a mill, for which purpose usually the so-called *pug-mills* are used, a kind of vertical mortar-mill, sometimes with revolving bottom dish, or, if the dish is stationary, with a mechanical arrangement for throwing out the mixture as soon as it has reached the proper consistency. The pyrites-smalls are thrown into the mill, water is run on, and the mill is run till a homogeneous mixture similar to fine mortar has been formed, which by itself has somewhat plastic properties. This mass is dried in layers of ½ in. thickness on the top of the pyrites-burners, often in cakes about 18 in. square; and after twenty-four or thirty-six hours it has hardened sufficiently for use. It is broken up into pieces of the same size as the lump ore, and charged together with this into ordinary pyrites-burners. In this case it is not necessary to observe a certain proportion; for the balls made in this way are so hard that they can be thrown to the ground without being broken; they do not fall to powder in the burners, and burn out as well as lumps; their cinders are, of course, of the same value as those from lump ore, whilst those mixed with clay make the utilisation of the ferric oxide, produced at the copper-extraction works, very difficult.

The principal drawback of the process is this, that the mills suffer very much wear and tear from the hard pyrites. In spite of this, it was formerly the most usual plan in the large English factories. The cost of labour for grinding, carrying to the top of the burners, for drying, taking down, breaking up, and laying down in front of the burners some years ago was 1s. 4d. per ton. To this must be added 6d. for coals for working the mill, and wear and tear of the same, altogether about 2s., apart from the wages for the burning itself (another 2s. per ton).

The process just described is not applicable in cases where the great bulk or the whole of the pyrites employed is in the shape of dust. In such cases formerly the only available contrivance was the above-mentioned muffle-furnace (p. 460), with all its great drawbacks. The first who proved that the heat generated by the combustion of ferrous bisulphide is sufficient for keeping the process going without any external aid, quite as well in the case of pyrites-smalls as in that of lumps, was Moritz Gerstenhöfer, whose furnace is described at length and shown in several diagrams in the first edition of this work, pp. 205-215. We here give only one diagram, Fig. 103, and a short description. That furnace consists of a shaft, 17 ft. high, 2 ft. 3 in long, and 2 ft. 7½ in. wide inside, provided with a large number of prismatic fire-clay bars, so disposed that the intervals of each upper tier are covered by the bars of the next lower tier. The pyrites-dust is fed in by means of fluted rollers, and drops from tier to tier, forcing down the particles previously lying on the bars according to the natural slope of the ore. Before starting the feed of the ore, the furnace is brought to a bright-red heat by means of a coal-fire. Afterwards the combustion of the pyrites by means of the air entering from below is quite sufficient for keeping up the heat.

The two great drawbacks of the Gerstenhöfer burner are: the very large amount of flue-dust produced in it, and the very incomplete desulphurisation of the ore (8 or 10 per cent. S in the cinders). Principally for these reasons this ingenious furnace has been abandoned again nearly everywhere, and is now only used for roasting "coarse metal" in a few copper-works. At the Freiberg works, where it was used for a variety of mixed ores (25 to 36 per cent. S), it has also been replaced by the Rhenania furnace, to be described below.

According to Scheurer-Kestner (*Bull. Soc. Chim.*, xlv, p. 228),

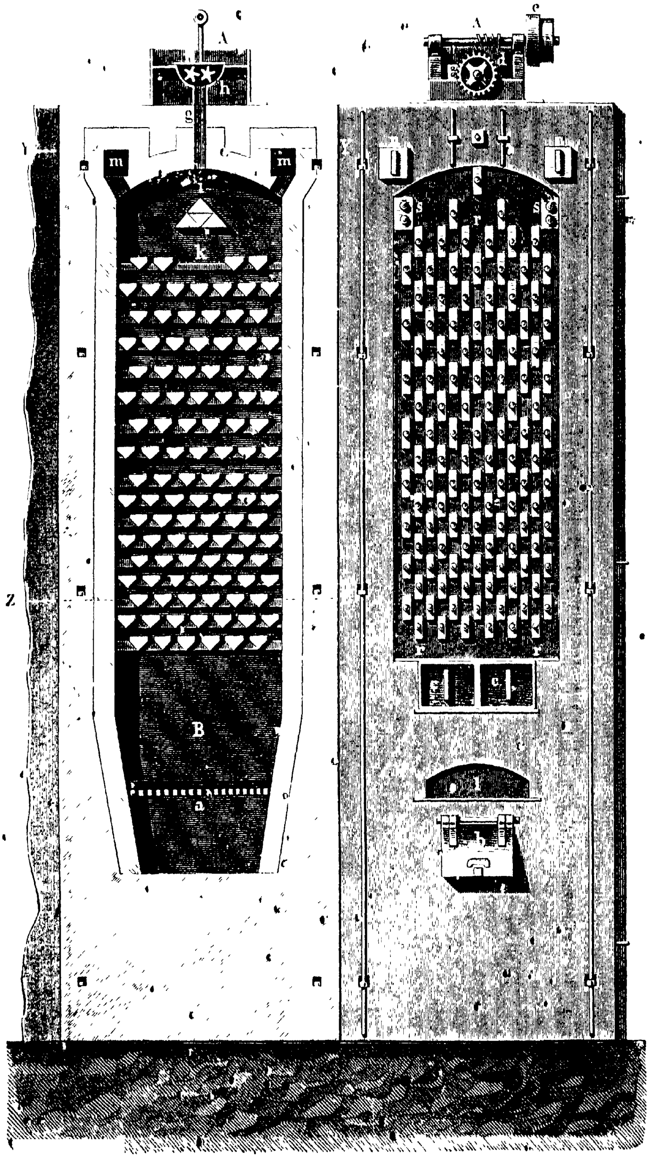

FIG. 103

Perret later on constructed a furnace, resembling Gerstenhofer's, but free from the defects of the latter. The pyrites was stated to be thoroughly utilised and the cost of labour reduced to one-half as against Malétra's "shelf-burners" (see below). At the time of Scheurer-Kestner's report the furnace in question was evidently still in the experimental stage; and as nothing more has been heard of it, its success cannot have been so great as anticipated.

The object but imperfectly attained by Gerstenhofer's invention has been realised by a very simple plan—so simple, indeed, that it was not thought worth patenting at the time, although it has subsequently proved to be of immense importance. Malétra owner of the works of Petit Quevilly, near Rouen, after having for some time burnt his smalls by means of an Olivier-Perret furnace, conceived the idea of separating the upper part of this furnace from the lower, and working the dust by its own heat of combustion without any aid from a lump-burner. This idea which was worked out about 1867 with the aid of Tinel, proved entirely successful; but in spite of this, and also of the "*shelf-burner*" being the simplest and cheapest of all dust-burners, it became comparatively slowly known; but since 1873, when it became better known through the Vienna Exhibition, it has spread on the Continent with extraordinary rapidity, whilst fo a long time it attracted little attention in England. The firs burner out of France seems to have been erected at the works o Schnorf Brothers, at Uetikon, near Zürich, in 1870; in Germany the first was erected at Kunheim's works in Berlin. Even if, a it would seem, some form of these simple shelf-burners had bee previously in use here and there, their *successful* application fo burning pyrites-smalls seems first to have been effected b Malétra's works.

Fig. 104 gives a longitudinal, Fig. 105 a cross section, th latter through two furnaces. Usually a whole set is built in row. In order to start it, a coal-grate, *a*, and fire-door, *b*, ar provided, which are walled up when the burner has got up to white heat. During this time the top working-door remain open. Then the five plates, *c*, *d*, *e*, *f*, *g*, are charged with smal ore through the doors *h*, *i*, *k*, whereupon the pyrites takes fire a once. The air enters through *l*, and is regulated at will. Th gas travels over all the plates in a serpentine manner, indicate by the arrows, escapes through *m* into the dust-chamber, *n*, and through *o* into the acid-chamber or into another dust-chamber. The chamber *n* is covered by a metal plate, *p*, upon which lead pans, *r*, *r*, are placed, in which all the chamber-acid can be concentrated from 112° to 144° Tw. The acid of one pan communicates with that of another (as usual) by siphons or by simple run-overs. Each of the shelves, which are 8 ft. long and 5 ft. wide, consists of eight plates in two rows of four each; they rest at the sides, in the walls of the burner, in the middle on fire-clay bearers, *s*, *s*, whose shape is better shown in Fig. 105. They are not equidistant, as can be seen in the drawing; the upper shelves, where more gas is evolved, are wider apart than the lower ones, where the radiant heat of the shelves is all the more useful. The best distance for the upper shelves is 4½ in. In order to burn a larger quantity of pyrites, it is not possible to leave the ore lying quietly, as in Olivier-Perret's burner, since here the external heating by the lump ore is

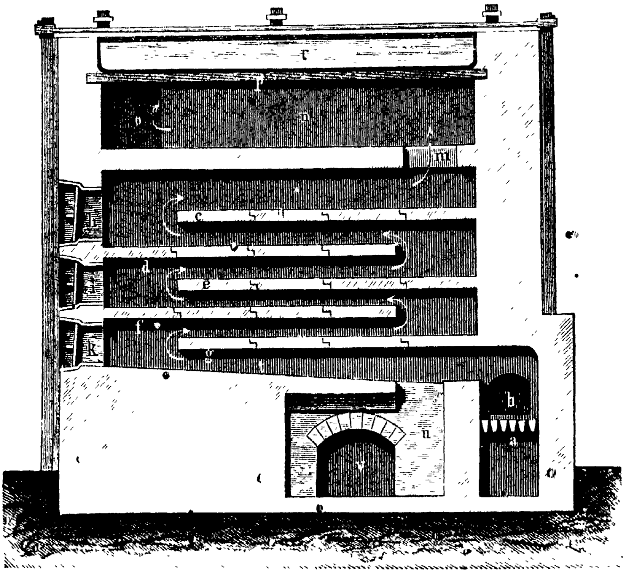

FIG. 104.

missing, the combustion would be too incomplete, and the heat would soon get so low that the burning would cease. The mass must therefore be turned over, which is done in the following way:—Every four hours the contents of the lowest plate, *g*, are drawn through the door *k* on to the arch *t* (which is level at the top, but slopes behind), after the burnt ore lying on the arch has first been pushed through the door *k* to the opening into the pit *u*. Then through the door *i* the contents of *f* are pushed down to the plate *g*, and there levelled again. Thus the higher plates are successively treated, till the highest plate, *c*, is emptied and can be charged with fresh ore. If four furnaces go together, one of them is on turn every hour. The contents of the pit *u* are removed once a day by the door *v*. The movement of the ore by removal from one shelf to another causes its thorough combustion, and thus also raises the heat. Four furnaces of the above dimensions burn daily 3 tons of pyrites. From 6½ to 7 lb. of ore are calculated for each superficial foot of shelving.

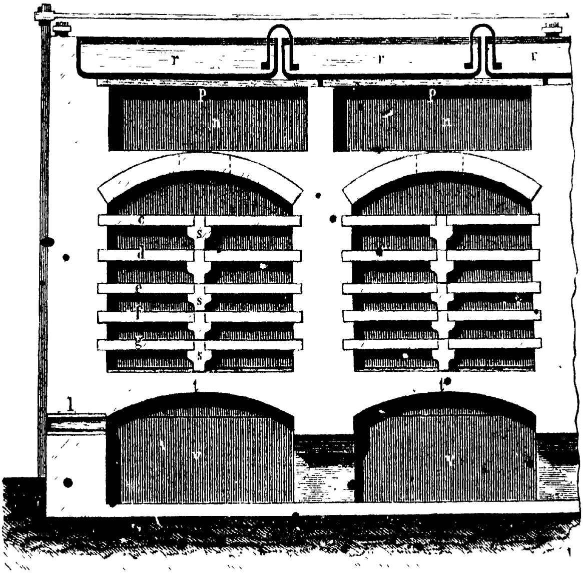

FIG. 105

Sometimes the shelves are made in the shape of a very flat arch, for the sake of greater stability; or at least the bottom is arched, especially in the case of wide shelves. Some prefer building the furnaces in such manner that the fire-clay slabs forming the shelves are nowhere enclosed within the brickwork of the walls; they are then more easily replaced when broken.

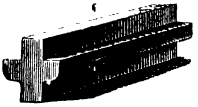

FIG. 106.

The Malétra burners were improved later on by making the fire-clay shelves stronger and doing away with the middle bearers, *s*, *s* (Fig. 106), which give much trouble in working the burner. These shelves are made from 3 ft. 3 in. to 3 ft. 7 in. inside.

Malétra's burner, which has obtained general acceptance in Germany, has been improved there by Schaffner, P. W. Hofmann, Bode, and others.

Through the kindness of Dr Max Schaffner, of Aussig, I was enabled to obtain detailed drawings of the shelf-burners as modified by him, and these are reproduced and described in our second edition, pp. 255 and 256. This furnace has seven plates, each served through its own door—three on one side, four on the other. On the first side there is also the ash-pit door, 18 in. square, for drawing out the cinders, which is thus done in the usual way, not by the rather inaccessible pit of Malétra. The doors all slide with their planed margins on equally planed ledges cast on the front plates, so that luting or plastering is not necessary. A certain number of angle-pieces are bolted to the front plates; these, between their outer bend and the planed ledges, leave sufficient room for the doors *t* to slide each way on the inclined face *a b*; and there is a sufficient number of such pieces present for each door to be always held by three of them (Fig. 107). This style of work is evidently much cheaper than casting everything in one piece, because the planing is much easier; it is also cheaper than the English style, shown on pp. 425 and 426, and quite as substantial as the latter. There are no special openings for the air, as, in spite of the planed surfaces, sufficient air enters to support the combustion. The regulation of the draught is here effected entirely by the chimney-damper.

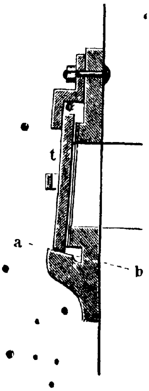

FIG. 107.

draught is here effected entirely by the chimney-damper.

In this burner *dust and peas* are burnt *together*, and the sulphur is burnt down to 1 per cent.; thus the grinding of the smalls, which is still practised at some works, is done away with.

The Aussig or Schaffner dust-burner has been erected in many works from the plans given in the previous edition of this book, and that with entire success. Of course at some places minor modifications have been introduced, but the principle is always the same, also in the plans given by Falding in *Min. Ind.*, vii. p. 668.

Most manufacturers now consider that burners worked from both sides allow too much false air to enter, and therefore prefer arranging two rows back to back. I am enabled to give full drawings of the most modern dust-burners from the designs of Mr H. H. Niedenfuhr, as shown in Figs. 108 to 110. They are clear enough to require no further description.

According to communications from Mr Benker in 1902, he still built his Malétra furnaces on the old system (p. 465), all the compartments in one line. On the top he places a collecting-flue and dust-chamber, 5 ft. high; at the end of the set a large dust-chamber, of the same height and width as the furnace and 20 to 30 ft. long, according to the description of ore. One man serves two compartments. Each of these burns 20 to 24 cwt. of 50 per cent. pyrites per twenty-four hours, but up to 32 cwt. of poor ore, such as he had to work in Italy, containing 26 per cent. sulphur and 3 per cent. copper, of which 90 per cent. was soluble in water and 95 per cent. soluble in dilute sulphuric acid after roasting. The ore is spread on the plates by means of a tooth-rake, producing an undulated surface and not leaving any bare places. From such poor ores Benker obtained gases with 7·7 per cent. SO_2 on the average, and produced 6·2 kg. acid of 106° Tw. per cubic metre (=0·39 lb. per cubic foot) in twenty-four hours, with a consumption of 0·7 parts nitric acid 66° Tw. to 100 sulphuric acid 106° Tw.

One of the principal advantages of the shelf-burners is that the ore is burnt out to a much larger extent not merely than with any of the older forms of dust-burners, but even with the best lump-burners. Even without grinding the smalls it is quite easy to keep the sulphur in the cinders down to 1·5 per cent. At many works, *e.g.* at Uetikon, the average amount of sulphur in the cinders never exceeds 1 per cent., and frequently it is below. At Malétra's own works they get down to 0·6 or 0·8 per cent., but this can be done only by crushing the smalls down to an almost uniform fine powder. The amount passed through the burner also influences this. Sorel states that a set of burners, charged with 34 or 35 kg. of ore per square metre every twenty-four hours, was regularly burnt down to 0·75 per cent.; with 36 kg. the sulphur in the cinders rose to 1 per cent., with 32 kg. it fell as low as 0·42 per cent. Jurisch, in his *Schwefelsäurefabrikation* (p. 80), quotes 30 kg. pyrites per square metre of plates, with variations from 25·6 to 35·8 kg. Stolzenwald (*Chem. Zeit.*, 1901, p. 22), when burning Hungarian pyrites (47 per cent. S), was not able to burn more than 24 kg. per square metre of Malétra plates, in order to get down to 1·7 per cent. S in the cinders.

I have seen in Germany shelf-burners working-up "peas" of Spanish ore down to 2·8 per cent. S, and even real "lumps" of Westphalian ore down to 3·5 per cent. S.

Such results can, of course, be obtained only with pure ores free from zinc, lead, etc. Hence the cinders from shelf-burners are readily bought by iron-works, both for blast-furnaces and other purposes.

The Malétra burner is particularly adapted to rich ores. With a 50 per cent. ore good results are obtained, if from 32 to 37 kg. ore is burnt in twenty-seven hours on each square metre of plate surface (*i.e.* 6·5 to 7·5 lb. per square foot). The lowest limit is 28 kg. (= 5·7 lb.), and this should be only exceptional because otherwise the burners cool down. For poor ores, that is below 38 per cent. sulphur, the shelf-burner is not well adapted.

In a six-shelf burner there ought to be scarcely any purple flame visible when pulling the charge down from the top shelf to the second shelf. The second shelf is at a bright red heat, the third one less so, and so forth; the back part of the fifth ought to be visible only at night by the light radiated downwards from the fourth, and the sixth ought to be perfectly black. Krutwig and Dumoncourt (*Chem. Zeit. Rep.*, 1898, p. 242) found the temperature on the top shelf = 680°, on the second 750°, on the third 720°, on the fourth 650° C.

Sorel found the following percentages of sulphur on the different shelves:—

Sulphur in green ore	50	per cent.
First shelf	32	,,
Second ,,	17	,,
Third ,,	7	,,
Fourth ,,	5	,,
Fifth ,,	2	,,
Sixth ,,	0·75	,,

He regularly found half of the sulphur in the cinders to be in the shape of FeS, the other half in that of ferric sulphate.

Crowder (*J. Soc. Chem. Ind.*, 1891, p. 298), in working with shelf-burners containing seven beds, charged once every eight hours (so that the charge takes 7 × 8 = 56 hours to complete the course), found the following percentages of sulphur on the different shelves (nearly agreeing with Sorel's results mentioned in the text:—

	Average of 23 trials.	Ditto of 26 trials.	
Ore charged	50	50	per cent. S.
No. 1 shelf	32·27	32·81	,,
2 ,,	21·41	17·55	,,
3 ,,	12·77	11·09	,,
4 ,,	6·39	5·05	,,
5 ,,	4·08	3·42	,,
6 ,,	2·35	2·56	,,
7 ,,	2·27	1·96	,,

If there is too much draught, the lower shelves cool down and the upper ones get hotter. This may cause the process to appear as going on very well; but it soon turns out bad. If, on the contrary, there is too little air, the bottom shelf becomes luminous and the sulphur in the cinders rises rapidly. In both cases there is incipient fusion on the second shelf, which prevents the roasting from being carried through. This can be remedied by admitting a little air at the door of the second shelf, or even mixing a little dead ore with the charge. The admission of air to the intermediate shelves serves also for bringing forward any burners which have got behind, and to burn any sulphur subliming from the first shelf, in case the burners are going too hot, or from damp pyrites giving off sulphuretted hydrogen; but this expedient, useful as it is when properly handled, must be employed, with caution lest the bottom shelves get too cold from want of air.

In the normal style of working all the air required for converting the sulphur into sulphuric acid enters at the bottom shelf, and this large quantity of cold air may lower the temperature of the nearly burnt-out mass to such an extent that no more ferric sulphate is decomposed. It was at first attempted at Malétra's works to avoid this by leading the burner-gas downwards underneath the bottom shelf, thus heating the latter and employing the ground-space as a dust-chamber; but this plan did not answer and was soon given up again. It has even been tried to utilise the heat of the burner-gases for a previous heating of the air serving for the burning-process. But evidently this must most seriously interfere with the draught, and will hardly answer in the long run. The same advantage would be secured more easily by admitting at the bottom only the quantity of air absolutely necessary for completing the roasting of the air, and allowing the remaining air to enter by a regulating-slide in the top working-door. In this case the bottom shelf will be visibly red-hot in the dark. This plan can be carried out only where the draught is very good, for instance by making the gas to rise to a considerable height before entering the chambers, and never leading it downwards in any part of its course. The burner walls should in this case be made thick or hollow to prevent loss of heat in the lower part; on the contrary, any overheating of the top shelf should be avoided by making the gas-flue rather high and causing the heat to be dissipated there, most rationally by means of evaporating-pans for sulphuric acid. Another plan is, introducing the requisite excess of air into the first chambers by means of an injector.

The management of shelf-burners is really easier than that of lump-burners, but it involves a little more labour. It is generally assumed that one man can charge, burn, and withdraw a ton of pyrites every day; but it is possible to get up to 25 cwt. It seems best to give five burners to each man, so that each burner is charged every five hours. The phenomenon of scarring (p. 449) is hardly ever noticed here. The working-doors must never be left open any longer than is absolutely necessary for the work; in this case both the yield of acid and the consumption of nitre are just as favourable when working dust on a shelf-burner as with the best lump-burners. This is the uniform testimony of the numerous works I have visited.

In order to start a new burner (which, of course, must have been thoroughly dried first in the ordinary manner), the communication with the chambers is stopped and a fire is lighted on the shelves, beginning with the bottom, sometimes by means of a temporary chimney. After four or five days, when the burner is moderately red-hot (it is unnecessary and even injurious to get it up to a *bright* red heat), the remainder of the fuel is cleared away, pyrites is charged on the three top shelves, and communication so made with the chambers, whereupon the regular service is started as previously described.

For some time past the shelf-burners have also been introduced into a number of English works, and everywhere with great success. This has been done on the largest scale at the Newcastle Chemical Co.'s Works (Allhusen's), where 129 shelf-burners on Schaffner's plan, described in this book, have been erected, which consume from 600 to 650 tons of pyrites-smalls (Mason and Barry's) per week. Each burner is charged, once in eight hours, with from $4\frac{1}{2}$ to $4\frac{3}{4}$ cwt. of smalls.

The objections made to the shelf-burner in its employment for sulphite paper-works by Harpf have been refuted by me in *Z. angew. Chem.*, 1896, pp. 65 and 157.

Combination of Lump-burners and Dust-burners for the Same Set of Chambers.—Such a combination is generally avoided, as the conditions of draught are very different in each case. I have, however, seen a combination of the above-mentioned kind in excellent operation at the Stassfurt potash-works managed by Dr Bernhardi, the good result being brought about by placing the shelf-burners so low that the top shelf is on a level with the charging-door of the lump-burners. This causes an upward draught in the shelf-burners, and prevents their blowing out, even when the doors are opened.

Other Descriptions of Shelf-burners.

The furnace of Finch and W., J., & S. Willoughby (B. P. 2913 of 1883) differs from a Malétra burner only in that the shelves, instead of being placed horizontally, are inclined alternately in opposite directions.

A modification of the Malétra burner has been patented by Mactear (3701 of 1878).

A furnace, combining some of the features of the Gerstenhofer and the Malétra burners, has been patented by Hasenclever and Helbig (description and diagrams, first edition of this work, pp. 220 to 222). It has never been carried out in practice, and is not likely to be so now.

E. Bramwell (Ger. P. 22758) has constructed a somewhat complicated pyrites-burner, in which, contrary to the ordinary dust-burners, the fresh air meets with the green ore, the products of combustion being gradually led over partially roasted ore, and at last over the almost spent cinders. This is effected by placing five calcining-beds in a row, each of them provided with an outlet for the gas connected with a gas-main, to be connected or disconnected by means of a throttle-valve, so that the current of gases can be directed at will. The last burner of the series communicates with the first by means of a flue underneath, so that a regular rotation can be kept up, as is done in lixiviating vats for black-ash.

Mechanical Dust-Burners.

The necessity of frequently opening the doors in Malétra's and all similar furnaces is certainly a drawback; it necessitates much labour and cannot but introduce some false air. These drawbacks have been overcome in a most ingenious way in the mechanical pyrites-dust burner constructed by MacDougall Brothers, of Liverpool; but, unfortunately, fresh troubles have arisen there which have caused these burners to be abandoned again. Still, as in theory they are the most perfect of all dust-burners, we will describe them here, especially since the drawbacks connected with them have been overcome by later inventions. The MacDougall burner is shown in Figs. 111 to 113.

The burner consists of a metal cylinder, 6 ft. in diameter and 12 ft. high, formed of seven rings, *aa*, bolted together, and provided with a solid bottom, but open at the top. The rings are cast in such a way that the lower and inner edge of each can serve as an abutment for one of the flat arches b_1 to b_6 which divide the inner space of the cylinder into seven chambers, the uppermost of which is open at the top. The

arches, as well as the cast-metal bottom of the cylinder, are pierced in the centre, and allow the passage of a cast-iron shaft, *c*, 6 in. thick, which is turned by means of the toothed wheel *d*, the pulley *e*, and the steam-engine *f*. The shaft carries at top and bottom the lutes *g* and g_1, into which the cups *h* and h_1, fixed to the top arch and the cylinder-bottom, enter; the latter are fast, whilst the lutes *g* and g_1 turn round with the shaft, and a hydraulic joint prevents the escape of gas at the places where the shaft enters and leaves the cylinder. To the shaft are fixed the cast-iron arms, i_1, i_2 . . . i_7, provided with teeth along their lower margin. The teeth are placed alternately in opposite directions; so that the arm i_1 moves the ore-dust from the centre to the periphery, i_2, the same from the periphery to the centre; i_3 acts like i_1; i_4 like i_2, and so forth. Corresponding to this, the arches are perforated alternately—b_1, b_3, and b_5 near the margin, b_2, b_4, and b_6 in the centre. The latter have a large central opening, 1 ft. 3 in. wide, lined with a metal pipe, which gives free play round the shaft to the gas and the ore-dust; whilst in the other arches the shaft is so tightly surrounded by a metal pipe that scarcely any dust, and still less gas, can get through. The small ore (which need only be passed through a 1-in. riddle, and therefore contains pieces up to the size of a walnut) is lifted by the elevator *k* (also moved by the engine *f*), and is emptied on to the top flat, b_1, where the arm i_1 takes it round and gradually moves it towards the periphery. During this time the ore is completely dried by the heat of the gas below. The ore dropping down the edge at *l* from the open top chamber is continually pushed into the first closed chamber by a ram at A. The ram A can be moved reciprocally either by the rod B or C, and can be moved more or less quickly, so that the feed of ore can be regulated to a nicety. The arm i_2 moves the ore towards the centre of b_2, where it drops down; i_3 moves it towards the periphery of b_3, where it drops down again, and thus quite gradually and constantly, being directed by the teeth of the arms, arrives at the bottom, and is emptied out through the pipe *m*. The two sides, *n* and *o*, allow the contents of *m* to be got out without any loss of gas or any air entering the other way. As the furnace during the operation is in full heat, most of all near the top, the ore ignites as soon as it arrives on the bottom of the first closed chamber, b_2; and in its gradual zigzag way towards the bottom the sulphur is completely burnt off. The air is continually supplied by the air-pump *p* in exactly the necessary quantity; and the gas escapes through the pipe *r* to the acid-chambers.

An apparatus such as is here figured is sufficient for burning 3½ tons of ore in twenty-four hours; with eight closed chambers instead of six, it can burn 5 tons. It is also very well adapted for burning the spent oxides of gas-works; but then it must have only four chambers. In a factory on the Tyne, where this apparatus was at work for a while, the consumption of coals for driving the engine amounted to 4 tons per week. A 2-h.p. engine and 1½ in. steam-pipe are said to suffice for the largest burner. The wages amounted to £4, 5s. per week; but this rather high amount was explained by the fact that two other furnaces were being built, which were expected to be served by the same men who attended the first. Of course this apparatus is quite independent of the skill of the burner-men, which is mostly acquired only after long practice.

For heating up, the engine is started and the cold furnace is gradually filled, care being taken to regulate the thickness of the layers of ore on the different floors. When the ore has arrived at the bottom, the engine is stopped, and the flame of a temporary fireplace, built against the cylinder, is allowed to enter it, until the ore lying on the bottom and the floor b_2 has taken fire. Then the engine is started, the temporary fireplace is taken away, the manhole is closed, and nothing remains but to see that the ore arrives at the bottom properly burnt. If this should not be the case, the speed of the feeding-ram A, that of the air-pump, or that of the agitating-shaft is altered till everything is in order. It is easy to get the sulphur in the burnt ore down to 1 per cent.; in forced work only 3 to 4 per cent. can be attained.

The objection might be made to MacDougall's burner that the machinery in its interior must wear out very quickly. In order to obviate this, all parts of the machinery are made of thick cast-iron; and, when one of the arms is worn out it can be replaced through the manholes, *s*, *s*, without allowing the apparatus to cool down. That otherwise this burner has many very great advantages over all others is evident. The turning over of the small ore is perfect without any opening of the doors and working by hand. Not even during charging and discharging does false air enter the burner; and by means of the air-pump exactly the necessary quantity of air can be admitted (this, however, in practice was found to be very difficult). This work, indeed, is done under such favourable conditions as are realised by no other burner, whether for pieces or for smalls; and it might be assumed that the consumption of nitre would thus be reduced to a minimum, and the yield of acid raised to a maximum. Nevertheless MacDougall's burner had to be given up again in the above-mentioned factory, because the quantity of flue-dust was so great that it could not be managed in any way, and the chamber-process was seriously interfered with. Taking the gases through a Glover tower was not to be thought of. It does not appear that really efficient dust-chambers were employed. The air-pump acted so violently that the dust was carried away a great distance.[1] Probably this drawback might have been counteracted by some alteration in the construction; but, altogether, the machinery caused endless trouble, continually requiring repairs, and there is no doubt that it would have to be altered a good deal before it could become a real success.

The drawbacks ascribed to MacDougall's furnace were intended to be obviated by a new patent of the same inventor, B. P. 3985 of 1883. He describes dust-chambers provided with perforated baffle-plates for the interception of dust carried over by the draught, arrangements being made for drawing out the settled dust without allowing gas to escape or air to enter. The shaft and rake-arms are constructed of cast iron, having a central wrought-iron tube so as to obviate warping or bending from the effect of heat; and in order that the shaft may be readily withdrawn, the arms, or rakes are fixed thereto by a fork-shaped end and cotter. A second modification is described, which is to avoid the dust occasioned by the vertical passage from floor to floor. The furnace is constructed as an oblong horizontal floor or chamber, provided with a series of vertical shafts, having rakes similar to those above described, and revolving in opposite directions. The teeth are so placed as to draw the material towards each shaft, and thus pass it from one to the other and from end to end of the furnace. Where prolonged roasting or burning is requisite, a similar furnace, or the first modification, may be superposed above the last mentioned, the material being first passed through the upper furnace.

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[1] Davis (*Chemical Engineering*, ii. p. 120) mentions that with mechanical draught out of 25 tons of dust burned per week 4 tons were carried away as flue-dust!

A further improvement was patented by the same inventor as B. P. 22504 of 1891. Here the central shaft is made in several lengths, coupled together by widening one end of the shaft to form a square socket, and fitting into this the square end of the other shaft, the two being secured by a square key wedged between socket and square end; a tight-fitting spring-clip protects the coupling from the action of the burner-gas. The furnace-rings are joined together by half-check joints secured by set pans and rust jointing; the ends of the pins are not exposed to the corrosive fumes.

The subject of mechanical furnaces generally has been treated in detail by Bode, *Dingl. polyt. J.*, ccxix. p. 55, and Wagner's *Jahresber.*, 1876, p. 296.

A furnace very much like MacDougall's was patented by Mr Perret in France, on 23rd June 1875.

A mechanical pyrites-kiln, greatly resembling MacDougall's in principle, was patented by R. Mackenzie (B. P. 4418 of 1881). It is provided with a water-cistern at the bottom, with the object of promoting the process by the presence of aqueous vapour. A similar furnace, differing only in details of construction, was patented by Black and Larkin (B. P. 4456 of 1881), and another by Johnson in America.

The ordinary shelf-burner has been combined with a mechanical arrangement by Hering (Ger. P. 9634), who feeds the top shelf continuously by means of a screw, the burnt ore being removed from the bottom shelf by another screw.

T. Mason (B. P. 3196 of 1880) employs a furnace with a bed slanting slightly downwards, across which a number of fluted rollers (say twenty) are lying, made of cast iron or stoneware, moved by means of gearing outside the furnace. The pyrites-dust is fed mechanically into a hopper, situated at the upper end, and is gradually moved down the inclined hearth by means of the fluted rollers, the cinders being discharged at the lower end. A furnace placed below gives additional heat in the case of poor ores. [It is not likely that such an arrangement would stand the wear and tear unavoidable in this case.] Modifications of this furnace are contained in the patent 1788 of 1881, and 2831 of 1882.

Walker and Carter (B. P. 4000 of 1883) employ for roasting pyrites a set of eight horizontal cylindrical retorts (four tiers of two each), heated outside by an ordinary coal fire, and communicating by openings at alternate ends. Hollow shafts, provided with stirrers, pass through each retort; cooling-water runs through all these shafts from one to another and prevents their warping. Special contrivances prevent the stirrers from touching the sides of the retorts in spite of unequal heating. The broken ore is fed into the top retorts and gradually finds its way into the three following tiers; a current of air traverses the retorts in the opposite direction. This apparatus is stated to have worked well for roasting pyrites containing 42·2 per cent. sulphur (*Eng. and Min. J.*, xxxvii. p. 294), but it does not convey the impression that it would go on for a long time without very heavy wear and tear; and the necessity of an outside fire also militates against it. The report made on this burner by W. Martyn (*J. Soc. Chem. Ind.*, 1885, p. 26) is not encouraging.

W. Bruckner (*Eng. and Min. J.*, xxxvii. p. 425; *Fischer's Jahresber.*, 1884, p. 221) employs for roasting pyrites-smalls a horizontal cylindrical revolving furnace. As this furnace is provided with internal firing, and the sulphur dioxide gets mixed with all the smoke-gases, it is hardly intended, and certainly not adapted, for serving in the manufacture of sulphuric acid. This is, on the contrary, the aim of an apparatus patented by R. and C. Oxland (B. P. 7285 of 1885), who roast the pyrites in a revolving cylinder of 30 ft. length heated from the outside, so that the SO_2 is kept apart from the smoke-gases. At the lower end of the rotating tube is a cast-iron prolongation, heated externally by a fire-grate and flues. The amount of air admitted to the calciner is regulated by a contrivance in the end plate of the prolongation, which is also fitted with a door for the removal of the cinders. (This apparatus seems to be more intended for roasting arsenical ores, and recovering the white arsenic in the process.)

K. Walter has constructed a special burner for "*peas*," that is, small pieces of ore between the size of a hazel-nut and such as pass through a sieve with eight holes to the lineas inch. This apparatus is described and figured in our first edition, pp. 225-229. It has grate-bars laid sideways across the burner, provided with projections beneath through which a bar passes. This makes it possible to turn all the bars at the same time and exactly in the same way. The spaces between the bars can therefore be made very small, so that the "peas" do not fall through without the bars being moved; and as they lie only 6 in. thick, the air can pass through with the ordinary draught. Each compartment, with a grate surface of 32 sq. ft., burns from 14 to 20 cwt in twenty-four hours.

Walter's burners require a strong draught, and must be worked for a separate set of chambers; with insufficient draught very large scars are at once formed. As they are only adapted for a special size of ore, they have not met with any extended application.

A very important modification is the burner constructed by Herman Frasch, which avoids most of the difficulties of the above system by the introduction of water-cooling. The Frasch burner has been described by me in *Z. angew. Chem.*, 1894, p. 15, from which parts of the drawings are reproduced here as Figs. 114 to 116. We notice the hollow shaft C, 8 in. outside diameter, 5 in. bore. Above the cylindrical burner it is connected with the fixed water-pipe D by means of a stuffing-box. As we see from Fig. 116, pipe *k* takes the water from the cistern E to the top of D, and pipe *k'*, starting from the bottom of E, reaches nearly to the bottom of shaft C. This causes a continuous circulation of water from E through *k'* downwards, then upwards in the annular space between *k'* and C, and back through *k* to E. Branch water-pipes reaching from C into the hollow stirrers H protect these also from fusing or deformation. Shaft C is, moreover, protected on the outside by wire gauze, covered with a paste of fireclay. The remainder of the figure can be easily understood by reference to the MacDougall furnace, but attention must be drawn to the very efficient dust-chamber shown in sectional elevation Fig. 114, and sectional plan Fig. 115.

I have convinced myself by personal observation of the excellent function of this apparatus, especially also of the fact

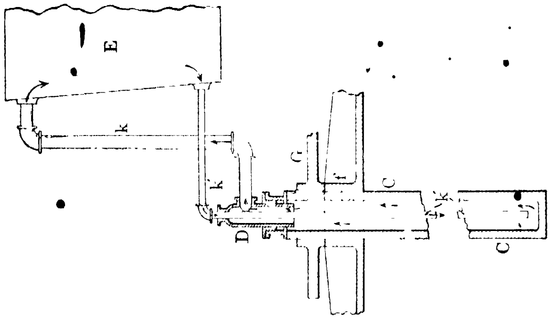
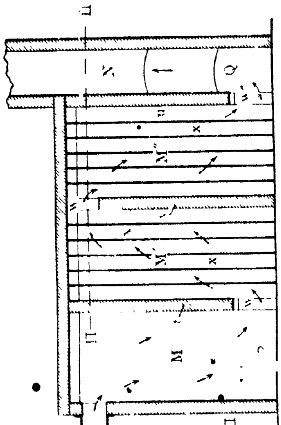


FIG. 116.



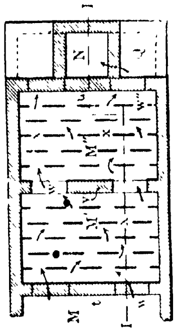


FIG. 115.

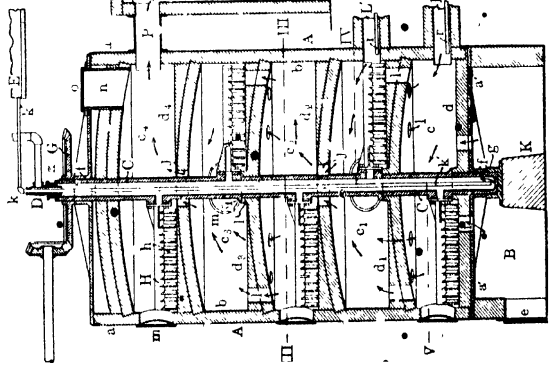


FIG. 114

that the protective water circulation between the hollow shaft C and the hollow side-arms H is quite sufficiently effected by the steam formed in the latter.

According to a report received from Mr Frasch, his furnaces, which are now regularly made 16 ft. wide, have done perfect work ever since; thirty of them are in operation at eight different works of the Standard Oil Co. for the purpose of roasting metallic sulphides. The heat produced in the interior of the shaft and arms is utilised by attaching a steam-drum to the highest portion of the water circulation, and the steam is used under 2 atmospheres' pressure for distilling benzine out of light petroleum oils.

The Herreshoff Burner.

Similar to the MacDougall burner is also the Herreshoff burner, but here the cooling is performed by air. The American patents of Herreshoff are:—Nos. 556750 (1896); 616926 (1899); 729170 (1903); 976175 (1910).

It is sold by the General Chemical Co. of New York, and the Metallurgische Gesellschaft of Frankfort. The former shape of this burner and its working are described in *Mineral Industry*, vi. p. 236, and by Gilchrist in *J. Soc. Chem. Ind.*, 1899, p. 460. That shape, with illustrations, is described in our last edition, vol. i. pp. 349-351. In the place of this we shall now describe and illustrate the burner in its recent shape, according to pamphlets issued by the General Chemical Co. of New York, and epistolary communications I have received from them.

The new Herreshoff furnace (Amer. P. 976175; Fr. P. 420975) is the direct result of an extended study in roasting the fines of ore. The irregularities of operations of fines' burners heretofore have sprung to a considerable extent from two causes. First slagging and sintering of the roasting ore which caught the arms and rabbles, sometimes breaking them, and an excessive dust production which necessitated cleaning of flues and consequent interruptions. The latter will be dealt with in a later part of this chapter, where the flue-dust is specially treated.

It was soon discovered that slagging and sintering, so called, was in reality a fusion of the FeS resulting from the distillation of half of the sulphur in FeS_2, that the fusion did not occur until after that sulphur was driven off, and that it did not occur when there was any amount of Fe_2O_3 present.

The problem immediately resolved itself into a regulation of the temperature of the roasting-ore between the points where the first atom of sulphur had been volatilised, and where sufficient iron existed as protoxide to prevent fusion by its reducing action.

This is accomplished by means of the cooling of the central shaft and arms, the amount of which can be varied in each arm, thus controlling the temperature of the roasting ore between the proper limits. It was found, when water was used as a cooling medium, that it was necessary to run through the shaft and arms sufficient water to prevent the temperature from reaching the boiling-point (otherwise it will form incrustations in the pipes), and this, as was soon found out, did not act as a cooling medium of sufficient elasticity. One might imagine that the slagging of ore could be prevented by cooling the entire furnace by means of decreasing the thickness of the brick lining of the shell, but here again the difficulty was encountered that with ores of lower sulphur contents the entire temperature of the furnace went down too much, and that the cinders resulting ran too high in sulphur.

The inventor finally settled on air as a cooling medium, because it is elastic and the quantity of heat extracted can be regulated. It is seemingly a wise selection. He also found that the lower hearth should be operated at as high a temperature as possible, for the presence of an excess of Fe_2O_3 prevents fusion, and the higher temperature will oxidise the remaining sulphur in the cinders more completely. In other words, instead of having, as formerly, the maximum temperature in the upper parts of the furnace, we now have it at the bottom. The construction employed to accomplish this appears in Amer. P., 22nd November 1910.

The new furnace consumes about $\frac{3}{4}$ h.p. in its operation, and revolves $\frac{1}{2}$ r.p.m.; it burns roughly about 10 lb. sulphur per square foot in twenty-four hours, with a cinder resulting which contains in the neighbourhood of 0·9 per cent. S., on any pyrite containing above 24 per cent sulphur, provided of course there is no copper, zinc, lime, etc., which will retain the sulphur in the form of sulphate.

The repairs on these furnaces are insignificant. The design is such that the temperatures of the cast-iron shaft and arms are maintained at about 800° F. = 427° C., at which point there is no condensation of acid, and the cast iron is at the point of maximum strength.

The only repairs which are found necessary are for the replacement of teeth which slowly wear by friction of the ore, and the best data obtained gives per annum a consumption of 140 lb. cast-iron teeth per roaster. It cannot yet be stated how many years the shaft and arm will last before the ordinary wear will necessitate their replacement.

The new Herreshoff furnace is shown in section in Fig. 117. It has a cylindrical steel shell placed vertically, lined with red brick, and in this shell brick hearths are placed horizontally one above the other. Passing down through the centre of these hearths is a double vertical hollow shaft. Attached to this shaft are one or more arms at each shelf, and replaceable rabbles, or teeth, are slipped on these arms. On one shelf they are placed at such an angle that the revolving arms plow and turn the roasting ore over in a regular way, making it travel from the centre of the hearth outward. From there it is discharged through proper openings on to the hearth below, where the teeth are placed at a proper angle to turn and plow the ore from the outside toward the centre of the furnace, where it again drops, as shown in the vertical section. This operation is repeated until the ore is finally discharged through an opening placed at the outer edge of the bottom hearth.

The life of the central shafts and hearths, as well as the teeth, is prolonged by internal cooling by means of air, which is forced into the bottom of the shaft, as shown in the drawings, and then delivered through the central shaft, from which it passes simultaneously at once into all the arms. After cooling the arms it returns into the annular space between the inner and outer shaft, and finally escapes at the top of the outer shaft.

The air for combustion is admitted over the lower hearth through ports in the outside shell and passes upward through the furnace in a counter-current to the roasting ore, escaping through the gas outlet.

Details of Construction.—The shell is double riveted and its thickness is proportioned to the size of the furnace. The brick lining is so arranged that the gases do not penetrate it and attack the shell. All seams are vertical.

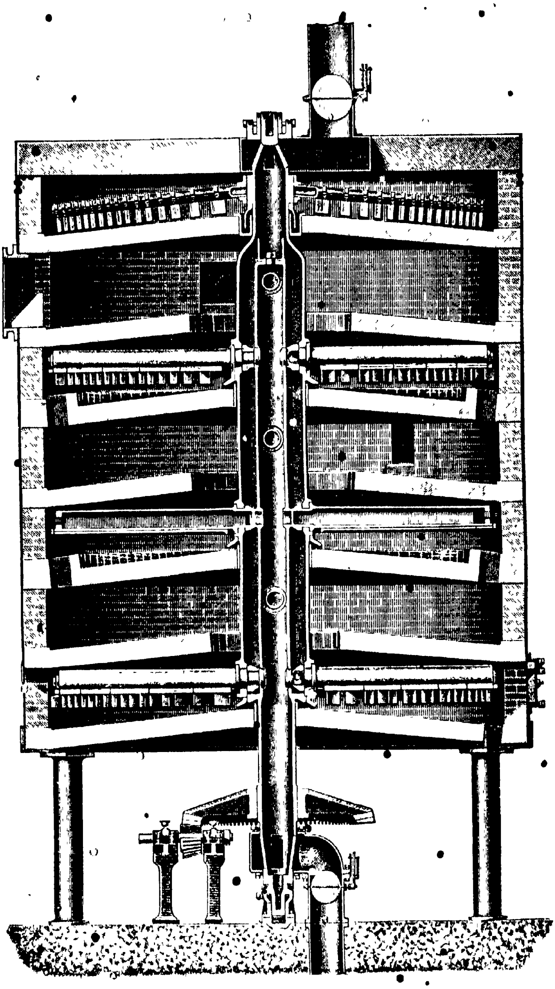


FIG. 117.

The hearths are of specially moulded arch fire-brick. The openings in the hearths for the passage of the gas and discharge of ore are carefully worked out to avoid the dust nuisance.

The shaft arms and rabble are made of close-grained special cast iron. The temperature of the iron in the shaft and arms is kept above the condensing-point of acid to prevent corrosion, and at a point where the strength of the metal is greatest. Either the bolted type or the bayonet-lock type of arm can be obtained. The rabbles are made in sections. There are five sections on each arm of from one to five teeth per section, depending on their position on the arm. The sections can be slipped on or off the arms, and any tooth can be taken out of the section and replaced without disturbing the remaining rabbles. Teeth and rabbles are made to template and fit perfectly in case of renewals. The shaft is driven from the bottom by means of a cast-iron gear and pinion, and makes one revolution in from 70 to 150 seconds, depending on the kind of roast. The six-hearth furnace, 15 ft. 9¾ in. diameter, requires about 1 h.p. Cast-iron doors, brick-lined to prevent corrosion, are fastened by two steel latches. The sight holes have heavy plugs hung on hinges, as shown in Fig. 118.

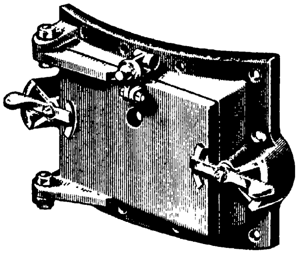


FIG. 118.

The new furnace is so designed that factories operating the old furnaces can have them converted to the new type (embodying the control and regulation features) without changing plant arrangements.

In the following table are given dimensions and data for some of the furnaces :—

	Outside diameter		Number hearth.	Hearth area	Weight metal parts	Weight special fire brick.	Pounds Sulphur per 24 hours.
	ft	in.			lb	lb	
Old Furnace .	11	7½	5	381	16,000	16,000	3,000 to 6,000
New Furnace .	11	7½	7	548	25,000	32,000	4,500 ,, 12,000
New Furnace .	15	9¾	6	912	43,000	79,000	8,000 ,, 21,000
New Furnace .	20	0	5	1308	68,000	132,000	12,000 ,, 30,000
New Furnace .	20	0	7	1810	82,000	168,000	16,000 ,, 42,000

In the above table the capacities given in pounds of sulphur per twenty-four hours must be used to form a general idea only, as the chemical composition and physical character of each ore, together with the kind of roast required (dead, magnetic or metallurgical), will have to be determined for each particular case before definite capacities can be estimated.

In general it can be assumed that capacities are lowest for dead roasting and greatest in metallurgical work.

Ores containing more than 20 per cent. sulphur can usually be roasted without the use of extraneous fuel. The furnace is started by heating up with gas, wood or other fuel, after which the ore is charged, slowly at first, then more rapidly, until the temperature in the furnace reaches the desired point. From this point the new furnace affords a remarkable regulation which, while preventing slagging, produces uniform results both in the strength of gas and the sulphur contents in cinder.

There were in 1911 over 1750 of various sizes of the Herreshoff furnace (1400 of these in Europe) in practical and economical operation in the following fields:—

1. Roasting pyrites for manufacture of sulphuric acid.
2. Roasting pyrites for manufacture of sulphite pulp.
3. Roasting pyrrhotite.
4. Roasting of mixed sulphides for magnetic separation.
5. Preliminary roasting of simple or complex sulphides for metallurgical work.

In roasting ores where extraneous fuel is required, such as zinc blende, ores for chlorination, or in the decomposition of telluride, a fire box can be added.

The furnace will be economical under such conditions, where the hot air from the central shaft can be used for the combustion of coal, oil, or gas and the consumption of fuel reduced.

These furnaces give no trouble whatever with granular ores, but with dusty ores, especially when used for lead chambers, they require one and a half as much dust-chamber space as hand-worked dust-burners, or the employment of a special dust-separator (see later on). In the case of contact processes and for sulphite pulp, where the gases have to be washed, they can be applied without reserve.

Hartmann and Benker (*Z. angew. Chem.*, 1906, pp. 1125 *et seq.*, and 1188 *et. seq.*) discuss at length the furnaces of Herreshoff, of O'Brien (p. 497), and of Kauffmann (p. 493), and the dust-chambers to be connected with them.

Up to the end of 1911 the Metallurgische Gesellschaft at

Frankfort had sold in Europe 1403 Herreshoff furnaces of the older type. According to *Chem. Ind.*, 1911, p. 561, there had been sold up to 31st March 1911, of end-furnaces: 357 in Germany, 102 in Great Britain, 116 in Austria-Hungary, 21 in Belgium, 10 in Denmark, 17 in Spain, 10 in the Balkan States, 147 in France, 3 in Holland, 237 in Italy, 15 in Portugal, 70 in Russia, 193 in Scandinavia, 2 in Switzerland, 512 in the United States

Other Mechanical Dust-burners.

Farmer and Hardwick's mechanical pyrites-burner (1878) resembles to some extent Jones and Walsh's mechanical salt-cake furnace (see our Vol II., edition of 1909, p. 192). It is automatically charged and emptied; 5½ tons of pyrites are said to be burnt off in from seven to nine hours. None of these furnaces seem to be in practical operation.

The mechanical pyrites-burner of P. Spence (patented in England, 24th December 1878; in Germany, No. 9267; in America, No. 248521) is a shelf-burner provided with mechanical stirring arrangement. As this furnace seems to be constructed on rational principles, and as it has met with practical success in America, we give a description of it.

Fig. 119 shows an exterior side view; Fig. 120 a plan; Fig. 121 a cross-section of one-half of a double furnace, the other half being shown in outside view; Fig. 122 a longitudinal section of the furnace-beds; and Figs. 123, 124, and 125 views of the stirring and raking instruments. The construction of the furnace-beds is best seen from Fig. 122. In this there are at 1 the walls of the furnace, in which are fixed projecting fire-clay slabs, 2. Upon these are placed tiles, 3, reaching from one side of the furnace to the other, a number of these composing the length of each furnace-bed. In Figs. 121 and 122 the several beds are shown at 3, 3*a*, 3*b*, 3*c*; alternate openings in these beds being shown at 4, 5, 6, 7. The pulverulent material is thrown at H on to the floor 3; advancing rakes or ploughs stir it and carry forward a portion of it through the opening 4 on to the second bed 3*a*. The teeth of the rakes are shaped with a triangular section, as shown in Fig. 125, the apex of the triangle being in the direction of the motion of each rake longitudinally from end to end of the furnace, the flat sides of the teeth of the

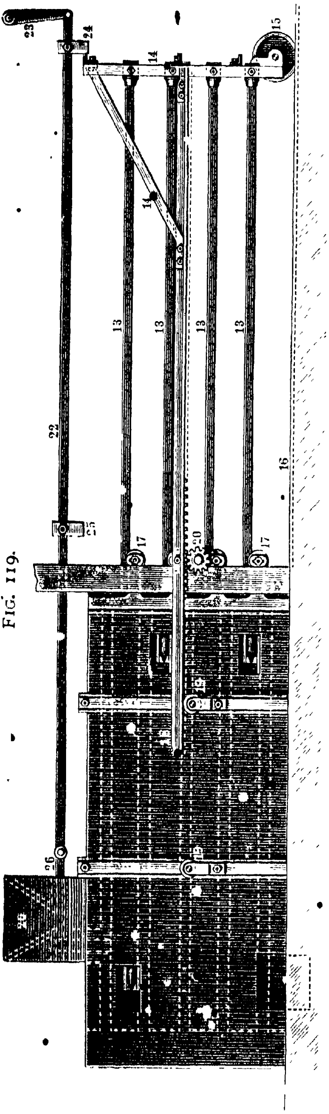


FIG. 119.

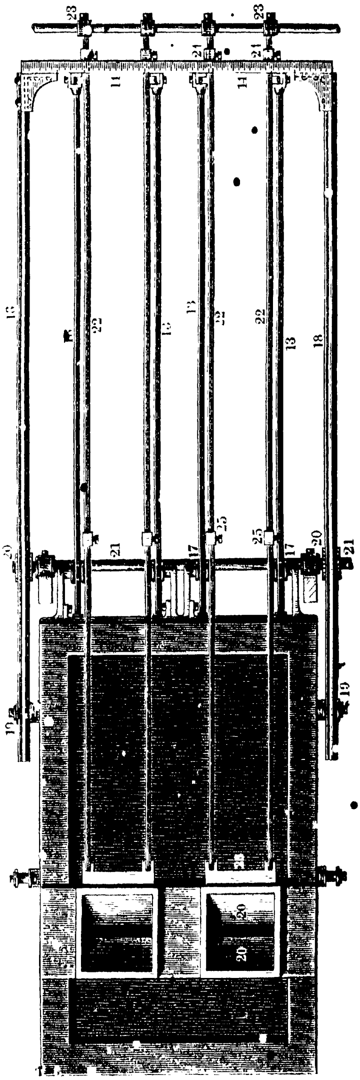


FIG. 120.

rake being in the direction in which it is desired to traverse the ore along the bed of the furnace. When the rake is advancing

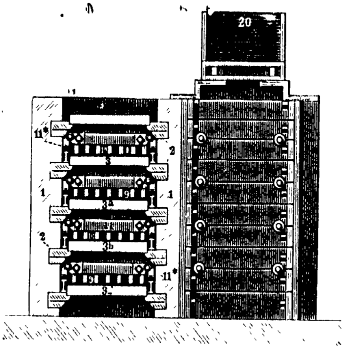


FIG. 121

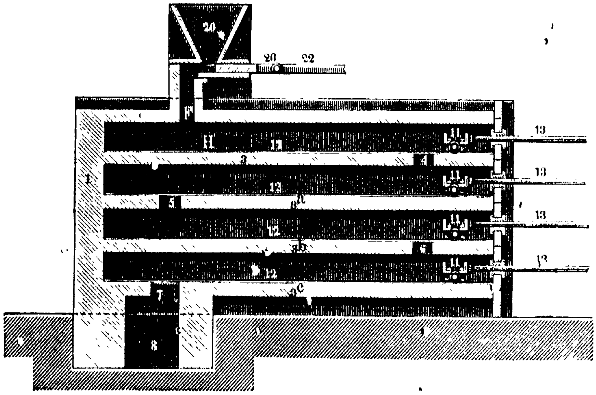
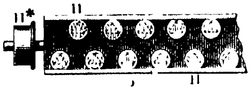
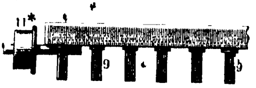


FIG. 122.





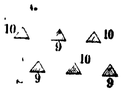


FIG. 123. FIG. 124. FIG. 125.

in the direction of the pointed part of the teeth of the rake, the ore will be only turned over; but when the rake is moving in an opposite direction, a certain quantity of the ore will be carried by the flat side of the teeth along the floor of the furnace. Thus the ground material, delivered to the floor 3 at the point H, is stirred and subsequently partially carried forward till it is delivered through opening 4 on to the second bed, 3*a*, where the same operations take place, the material now passing down the opening 5 on to the bed 3*b*, and so through all the beds, until it is at last discharged through the opening 7 into the receptacle 8. Since the openings in the successive beds are on alternate ends of the furnace, the stirring and conveying instruments must be reversed, as regards their faces, in succeeding beds. The teeth of the rakes are mounted in angle-iron bars, 11, provided with rollers, 11 *, which run upon rails, 12, carried by the projecting supports, 2. To each of these angle-bars are connected rods, 13, attached at their other ends to a frame or carriage, 14, provided with wheels, 15, which run upon rails, 16, on the floor, the said rods being supported and guided by grooved pulleys, 17. On the carriage, 14, are fixed toothed racks, 18, situated outside the furnace, and supported at their outward ends by rollers, 19, and in gear with these rods are pinions, 20, on a shaft, 21, driven by motive power. Motion being communicated to the shaft, 21, the pinions, 20, cause the racks, 18, to traverse the frame, 14, which, as stated, travels on the rails, 16, and thus the rods, 13, are caused to traverse the rakes or conveyers along the several beds of the furnace. According to the positions shown in the drawings, the carriage, 14, is in its outward, or nearly outward, position, and the flat ends of the instruments will have delivered a certain amount of material through the opening 4 on to the bed 3*a*, the same operation having taken place with regard to the opening 6 and bed 3*c*. The carriage now running inward, the sharp points of the ploughs will simply stir the material on the beds 3, 3*b*, while the blunt ends on the floor 3*a* will deliver a certain quantity of material through the opening 5 on to the bed 3*b*, and at the same time the instruments on the floor 3*c* will pass an amount of completely calcined material into the receptacle 8, to be removed at pleasure. The feeding of the furnace takes place in the following manner:—At F is a channel leading to the top floor, 3, and above this channel is a hopper, 20, into which the ground material is from time to time fed. The bottom of this hopper is provided with a sliding plate, 26, having a ledge at its inner end, as seen in Fig. 122. This plate is connected with rods, 22, swung upon arms, 23, and each having two stops, 24, 25. According to the position shown, the material rests upon the ledge of the plate, 26, which, when the carriage runs in, is pushed forward by its arrival in contact with the stops, 24, and this action delivers a certain amount of material through the channel F. On the return motion of the carriage the stops 25 shift the plate 26 back, and so on. Instead of plate 26, there may be a winged bottom to the hopper. The furnace may be single or double, the latter (which is shown in the drawings) being preferred. The shaft, 21, is connected by means of suitable gearing to any source of motive power, so that it may be rotated first in one direction and then in another, and thereby traverse the rakes alternately from one end of the furnace to the other. The rakes may move continuously; but it is preferable that they should remain stationary periodically in the position shown in the drawings, as they are then clear of the ore and out of the direct action of the heat, thereby suffering less injury from corrosion.

A number of these furnaces have been put up by the Sulphur Mines Co. of Virginia, at Baltimore. According to a communication made to me by the President, Mr Crenshaw, three double furnaces were connected with a set of chambers of 180,000 cub. ft. capacity, with Glover and Gay-Lussac towers, and two other furnaces with a set of 126,000 cub. ft. The five furnaces were to burn 14 tons of 47/48 per cent. pyrites each twenty-four hours, down to less than 2 per cent. of sulphur in the cinders.

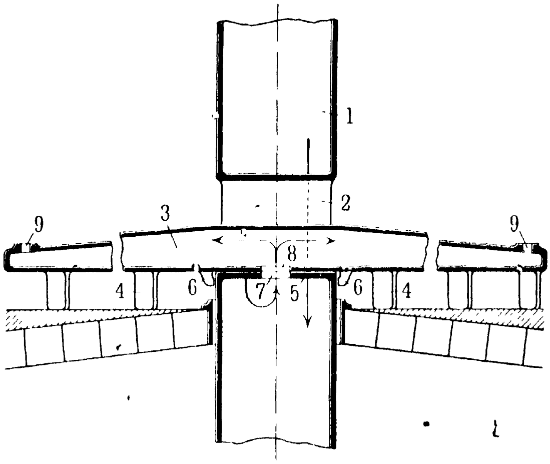
It is mentioned as a drawback of Spence's furnaces that at the back end a collection of dust takes place, by which the rakes are prevented from doing their work properly. Bartsch, of Bridgeport (*Fischer's Jahresber.*, 1886, p. 256), consequently applies to the furnace ends a separate set of broad plates, moved by a second moving-frame, in such a way that the dust is cleared out automatically every time the principal frame is made to work.

As stated in *Z. angew. Chem.*, 1894, p. 134, I have met with several Spence furnaces at work in America, but the opinions as to their advantages were divided. A modification of this furnace has been patented in America by A. C. Johnson, of Baltimore, where the moving parts are protected from heat (Amer. P. 642334).

Luty in *Z. angew. Chem.*, 1905, p. 1353, quotes results from actual practice, according to which, under European conditions, mechanical burners work less economically than hand-worked burners; but he thinks that with higher wages the cost may be the same, and then mechanical furnaces have the advantages of requiring fewer men and being less dependent upon them.

E. W. Kauffmann (*ibid.*, p. 1628) contradicts these conclusions, and maintains that mechanical pyrites roasting with modern furnaces, quite apart from the better result, is considerably cheaper than roasting by hand-work. At all events he claims this for his furnaces, which were for some time built by the Humboldt Engineering Works at Cologne, and are therefore sometimes erroneously called "Humboldt burners." His Ger. P. 161200 of 1903 describes a mechanical stirrer, with a hollow shaft, with a cooling agent flowing through it, provided with perforations for putting in the stirring-blades. These blades are of a special shape which allows the cooling agent to pass through them as well. Fig. 126 shows this arrangement in vertical, and Fig. 127 in horizontal section. 1 is the hollow shaft, which for each of the shelves of the furnace is provided with a rectangular channel, 2, of such a height that the hollow stirring-blade, 3, with its teeth, 4, can be put through; the width of the channel corresponds to the thickness of the blades. When in use, the arm, 3, rests in its central part upon the bottom plane, 5, of channel, 2, and is secured against shifting by the lugs, 6. A perforation, 7, is provided in the bottom plane, 5, of the channel, and a perforation, 8, in the plane of the blade resting upon it, so that the cooling agent, introduced under pressure, also penetrates into the hollow blades and gets out through the openings, 9, into the furnace. In this way also those parts of the blades which are at some distance from the cooling places, *e.g.* the teeth, 4, are protected against damage by heating. The Kauffmann furnaces are claimed to be mechanically far superior to the Herreshoff furnaces; they are built by the Erzröst-Gesellschaft in Cologne. The cooling agent is cold air, which is blown in by a fan-blast into the hollow footsteps of the shaft, in such quantity that it protects the blades against overheating, without interfering with the roasting-process. Each furnace roasts 2½ to 3 tons of 50 per cent. pyrites in twenty-seven hours, down to 1 or 2 per cent., with an expenditure of only ½ h.p., and requires no manual labour except for carting the ore and taking away again the cinders. A set of five such furnaces costs about £2500, including the steam engine, shafting, tubing, and dust-chamber, and the cost of erection. There is only one man required for looking after it and greasing the moving parts. The repairs are amply covered by £50 per annum.

FIG. 126.



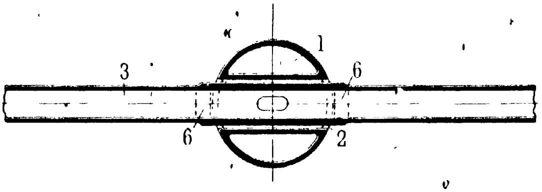


FIG. 127.

The other patents of Kauffmann are: Ger. Ps. 161624; 163914; 165270; 186314; 186315; 205215; 227621.

The Erzröstgesellschaft (Austr. P. 51096) states that the amount of work done by these furnaces can be largely increased by frequently turning over the ore, and gradually moving it forward in a radial direction. For this purpose the teeth of the stirring-arms stand alternately in opposite directions, so that the ore, moved forward by one-half of the arm, is brought back through part of the way already made.

Reusch (*Chem. Zeit.*, 1912, p. 213) states that in the beginning of 1912 about 600 such furnaces were working in Europe, America, and Australia.

Hartmann and Benker (*Z. angew. Chem.*, 1906, p. 1188) assert that the asbestos screens in the Kauffmann burners are destroyed after a short time.

The Pennsylvania Salt Manufacturing Co. at Philadelphia (for Europe the Metallurgische Gesellschaft in Frankfort) has introduced the mechanical pyrites-burner of Utley Wedge (patented in all countries; in United States as 648183; 649183; 654335; 777577; 842736; 976525), of which Fig. 128 gives a section, showing the salient features. The principal of this is the hollow revolving shaft 4 ft. inside diameter, to which the stirring-blades or arms are attached, and which is easily accessible for men from the inside. The two opposite arms are secured by bolting them together in the hollow centre, and are thus not exposed to the flame; they are rendered durable by cooling them by means of a current of air, produced by a fan, the only escape for the air being through the arms and thence out through pipes in the interior of the vertical shaft. This is made of ½ in. steel, protected from the flame by an exterior covering of bricks, supported on cast-iron rings. A cast-iron lute, filled with fire asbestos, makes a tight joint without necessitating any machine work on the furnace arms. A diaphragm in the centre of each arm forms a passage-way for the air (or water) along the bottom and back along the top of the arms so that this is effectively cooled. The entrance of the cooling-air takes place at the bottom, confined by a hood and lute. The hot air, having passed through the arms, is collected by another hood and allowed to escape into the atmosphere. The rabble teeth, which are the only parts exposed to the burner gases without cooling, are readily removed by reaching in from the exterior of the furnace, without stopping the furnace. A furnace of 20 ft. diameter roasts 12 tons of pyrites in twenty-seven hours and requires 1½ h.p. driving power.

There are six feeding-spouts in the top arches which divide the material evenly. The material descends in the furnace, first

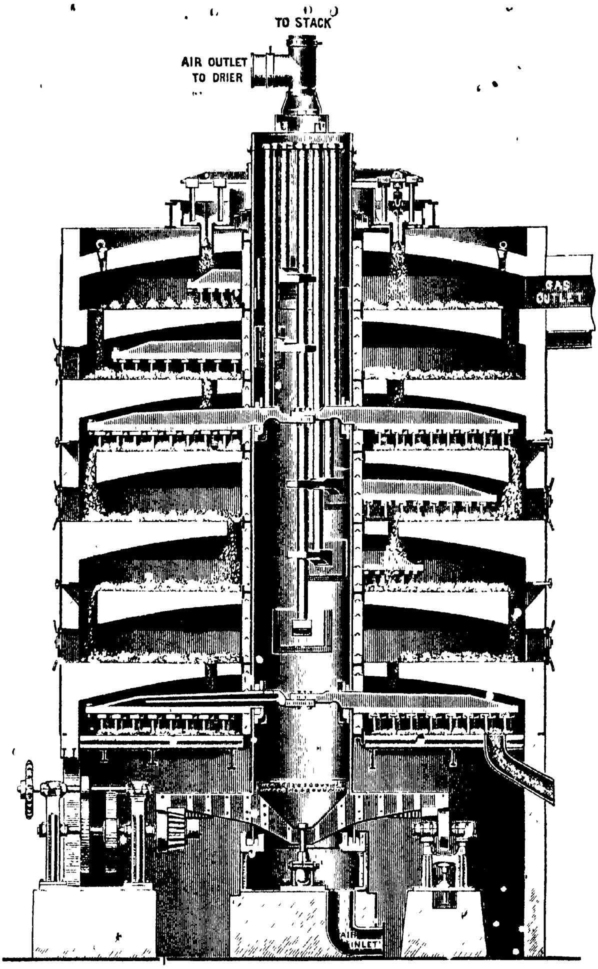


FIG. 128.

outward and then inward on alternate floors, and is met by the ascending air. The drop holes connecting these floors can be cleaned by means of poke holes through the shell of the furnace. The outer shell of this is one ½-in. steel. These furnaces are in full work at some of the leading American and European factories.

Improvements in details of these furnaces are protected by Ger. P. 243325.

For very large works the Wedge furnaces are specially adapted, whilst for smaller factories the Metallurgische Gesellschaft still sells many Herreshoff furnaces (*supra*, p. 484). At Philadelphia 6 such big furnaces are attached to lead chambers of a capacity of 1,000,000 cub. ft.; they roast together 100 tons ore in twenty-seven hours (Quincke, *Z. angew. Chem.*, 1910, p. 1922).

According to Hasenclever (*J. Soc. Chem. Ind.*, 1911, p. 1291) there were, in Germany, Wedge furnaces working satisfactorily in five chemical works and another 15 furnaces in course of construction. The largest type of them gets through about 20 tons of pyrites in twenty-seven hours each, that is six or seven times as much as the Herreshoff furnace, and their design is more compact and simple than that of the latter; but there seems to be no particular economy in cost of construction or working-expenses. The main feature of the Wedge furnace is that it permits of repairs being made without interrupting the working.

From private information I can add that in the beginning of 1912, 25 Wedge furnaces had been sold in Europe by the Metallurgische Gesellschaft, the smallest size burning 12 tons, the largest 20 tons 48 per cent. pyrites in twenty-seven hours.

The O'Brien furnaces, built by the American Coke & Gas Construction Co., very much resembles the Herreshoff furnace (p. 484). In this furnace the arms are put in and taken out horizontally and without raising. It is claimed that it requires less power than any other furnace of similar capacity, and is equally efficient for "fines" and for "granular ore"; the feed can be exactly regulated and the depth of the ore can be maintained differently on the different shelves, a shallow bed being used where the combustion is most active, and a deeper bed where the sulphur is partially burnt out. The central shaft is hollow, and no stack is required to create a draught through it; it can be easily withdrawn and replaced in a short time. The driving-mechanism is placed near the circumference of the furnace, where it can be easily reached for oiling and repairing.

Winteler (*Chem. Zeit.*, 1906, p. 457) discusses several burners for pyrites smalls, without any original work in that direction.

Simons (Ger. P. 166569) describes a mechanical burner for pyrites smalls, in which shaking-rods are placed on the grate-bars which alternately cover and uncover the spaces between the fixed grate-bars.

Howard (B. P. 21762 of 1905) utilises the waste heat of mechanical desulphurising furnaces for drying the incoming material on the top arch, with mechanical stirring, and thence feeding it into the interior of the furnace.

Legge (B. P. 21160 of 1905) describes furnaces containing two or more superposed series of roasting-chambers, with horizontal or slightly inclined hearths; rubble shafts with arms passing through them convey the ore through all the chambers of a series, and means are provided for discharging the ore.

The Maschinenbau-Anstalt Humboldt at Kalk (B. P. 27061 of 1906) forms each stirring-arm as a two-armed lever, and supports it on the shaft in such manner that it can be easily disengaged.

Timm (Ger. P. 195670) patents a mechanical muffle-furnace, without mechanical stirrers.

Greenaway (Ger. P. 182409) describes a mechanical pyrites-burner, consisting of a long hearth, with a stirring carriage over it, the hearth being formed by a porous layer of ore, divided by intermediate walls into several compartments, corresponding to the varying quantities of air required for the successive stages of the roasting-process. Each compartment possesses an opening leading to a vault in front, by which air is introduced and from which the porous layer may be renewed.

Merton (Ger. P. 185003) describes a special method of cooling the hollow shafts of mechanical roasters.

A mechanical dust-burner, with scrapers travelling backwards and forwards, has been constructed by Hegeler (*Min. Ind.*, 1905, p. 246), and is employed in a few factories, both for lead chambers and for the Schroeder-Grillo contact process. Here the stirrers are always conveyed to one side, are turned round there and conveyed to the other side again. The ore is dropped gradually from one shelf to the other once per hour.

Ducco's furnace (described by Hartmann and Benker in *Z. angew. Chem.*, 1906, p. 1194; Ger. P. 185809) consists of a horizontal wrought-iron cylinder, lined with bricks, with screw-shaped grooves for turning over the material, and shifting it gradually to one end of the cylinder, where it is discharged.

The Eisenwerk Laufach (Ger. P. 185673) effects the preheating and mixing of pyrites-smalls, previously to roasting it, in a slightly-inclined revolving tube, provided inside with screw-shaped scrapers. The pyrites passes in at one end, the preheated dry air at the other. This pre-heating is effected by previously passing the air through the hollow shaft in the centre.

Warren (B. P. 17457 of 1905; Amer. P. 864816) divides a rotary kiln into compartments by a hollow lateral partition, communicating with the air at diametrically opposite points. The hollow space diverges at opposite ends, where it communicates with the air. The other portion of the kiln forms a common chamber, the flame from which passes simultaneously into the compartments of the first portion.

Pfaul (Ger. P. 177963) feeds the burners in a regular way, especially in the case of employing pyrites-smalls of various degrees of moisture, by means of a hopper, provided with a central shaft, with an arrangement for brushing the sides of the hopper, and a feeding screw at the bottom, which at every revolution takes out the same quantity of ore.

Kuhrke (Ger. P. 159613) roasts the ore in a horizontal revolving drum, provided with three superposed screw channels, through which the ore passes gradually from the (centrally arrayed) inlet to the outlet at the bottom.

Falding (B. P. 6931 of 1905) provides for the stirring-arms means of being readily removed without removing the central shaft; both this and the arms are provided with an arrangement for cooling by air.

Wocke (Ger. P. 210657) employs a furnace with screw-shaped beds, each of them provided with entrance and exit pipes, on which stirrers move the ore on in a suitable manner.

Schlippenbach (Ger. P. 225421; B. P. 28755 of 1909; Fr. P. 415920) describes arrangements for conducting roaster gases of different composition to different gas-chambers, in such manner that each gas-chamber receives a continuous current of gases of similar composition. He employs an annular roaster, turning on a vertical axis, the space below which is divided into several compartments, each of them provided with outlet pipes.

Daniel and Romer (Ger. P. 208354) describe a roaster consisting of revolving drums superposed over one another, through which the ore is automatically propelled.

Collet and Eckardt (Norw P. 20273) bring the air, the burner gases, and the pyrites into contact in such a way that the burner gases containing most SO_3, with excess of air or oxygen, pass through the most highly roasted ore, in order to obtain a mixture of but little SO_2 with the greatest possible quantity of SO_3.

Zelewski (Ger. P. 195724 and Ger. P. appl. Z5379) describes a modification of the Herreshoff mechanical roaster (p. 484) in which the stirrers of the bottom compartment are placed in a special socket, surrounding the perpendicular shaft, so that a certain portion of the ore can be completely roasted off, while another portion lies still.

J. L. Tafto (Amer. P. 891116; Ger. P. 207760) equalises the SO_2 contents of pyrites-kiln gases, to obtain a product with 6 per cent. SO_2 and about 816° C, by passing them through an iron-cased brick, dust chamber and then through a similar chamber, packed with bricks, which is large enough to contain the gases for some time and to equalise the variations of composition, and temperature. Between these two chambers air can be introduced by means of a regulating-valve, and the gases containing too little SO_2 and too much O can be enriched in SO_2 by passing them to a layer of hot pyrites, where more SO_2 is generated.

St Beuve and E. Marconnet (Fr. P. 390323) blow finely ground pyrites by a current of air continuously into a combustion-chamber, provided with an exit opening for the SO_2, and a discharge opening for the removal of the residue. The pyrites, which may be mixed with substances for accelerating the combustion, or fuses, is delivered by a screw-conveyer into a chamber, and taken out by a fan, delivering it into the combustion-chamber by a tangential pipe.

Olga Niedepfuhr (Ger. Ps. 239702 and 239703) provides mechanical roasting-furnaces in their hottest parts with cooling-channels; cold roasting-gases are conveyed through the shaft and the stirring-arms. Easily and badly roasting ores can be worked in the same furnace, by putting them alternately into successive roasting-compartments.

Special contrivances for charging the ore into the furnace in a regular way are described by the Metallbank and Metallurgische Gesellschaft (Ger. P. appl. M42726) and by the Maschinenbauanstalt Humboldt (M43170).

The Svovlsyre and Superphosphat-Fabrik, Copenhagen (B. P. 28703 of 1911), describe a mechanical pyrites-roaster, provided with complete water-cooling of the shaft and all the stirring-arms, worked by a water-tank at the top, into which the exit-water pipes from the shaft and the arms are conducted back.

Other modifications are patented by Scherffenberg and Prager (Ger. Ps. 329759 and 332056); Lütgens (Ger. P. 358443); Hommel (Fr. P. 384350); Akttengesellschaft fur Bergbau, Blei- und Zinkfabrikation (Ger. P. 202377); Merton (Ger. P. 185506); Bracq-Laurent (Ger. P. appl. B52846); Grunewald and Welsch (Ger. P. 232044); Bragg and Moritz (Ger. P. appl. B52486); Parent (Fr. P. 424269); de Spirlet (Ger. P. 236089); Scherfenberg (Ger. Ps. 236090 and 237215); Hubner (Ger. P. 236669); Havris (B. P. 23331 of 1910); Renwick (Amer. P. 981880); Hardingham (B. P. 19314 of 1911).

C. SULPHUR DIOXIDE FROM ZINC-BLENDE AND OTHER SULPHIDES.

Zinc-blende is now the most important of all zinc-ores, and must be always converted into zinc oxide by a thorough roasting. This is nothing like so easy as with pyrites, since, on the one hand, blende contains at best only about 33 per cent., sometimes down to 18 per cent., of sulphur, and, on the other hand, it is much more difficult to burn out than iron or copper pyrites, zinc sulphate being formed, which is very difficult to decompose. As the manufacture of zinc requires that nearly all the sulphur should be driven off, and as the burners employed for pyrites are useless in the case of blende, the latter was formerly roasted in reverberatory furnaces, all the sulphur dioxide passing away with the furnace-gases. This would probably be done even now, if the damage produced by the acid smoke had not caused the sanitary authorities, both in England and on the Continent, to impose upon the manufacturers the duty of doing their best to condense the acids contained in the smoke, the damage caused by which has been described, *suprà*, pp. 269 *et seq.*

The development of the processes for abolishing the acid-smoke nuisance and utilising the sulphur in connection with the roasting of blende, at least in one of the most industrial parts of Germany, has been described at length by Robert Hasenclever (*Z. Verein. deutsch. Ingen.*, 1886, p. 83; *Fischer's Jahresber.*, 1886, p. 257), of whose paper we give a short abstract. Before 1885 all the blende consumed at the large Stolberg zinc-works was roasted in ordinary open furnaces by a direct coal-fire, the gases from which contained only about 0·75 per cent. SO_2 by volume and escaped into the atmosphere. In 1855 the Rhenania Chemical Works at Stolberg erected a furnace, intended to utilise the larger portion of the SO_2. This furnace, the invention of Friedrich Hasenclever, was the first by which the gases from roasting blende could be utilised for the manufacture of sulphuric acid. It consisted of a long muffle-furnace, in which the ore was shifted along the hearth from back to front by manual labour. Thus half the sulphur could be utilised for the manufacture of sulphuric acid, but with great waste of nitre. Godin improved this furnace by placing a series of muffles on the top, which the ore had to pass gradatim; but this apparatus was given up again for the Gerstenhofer furnace (*suprà*, p. 463). By this comparatively rich gases were obtained, but the immense quantity of flue-dust was very troublesome, and it proved too difficult to combine this furnace with another for finishing the roasting. After this several arrangements were tried by Hasenclever and Helbig, but these showed various drawbacks; and this led in 1874 to the construction of a new furnace, which has been fully described and illustrated in the first edition of this work, pp. 201-204; we describe it only briefly here (Fig. 129). It consisted of a reverberatory furnace, *g*, on the top of which was placed a muffle, *c*, reaching all over its length. The bottom of this muffle, forming the top of the reverberatory furnace, was heated directly; the flame of the furnace passing over the roof of the muffle heated this as well, and then passed under an inclined plane at an angle of 43°, at the top of which, at *a*, the fresh (powdered) blende was fed in. The ore, on sliding down this plane (partitions, *d*, *d*, preventing its transit from becoming too rapid), underwent a preliminary heating by the hot gases passing underneath; this heating was continued in the muffle *c c*, where air was admitted and as much of the sulphur was burned away as possible. At last the semi-burnt

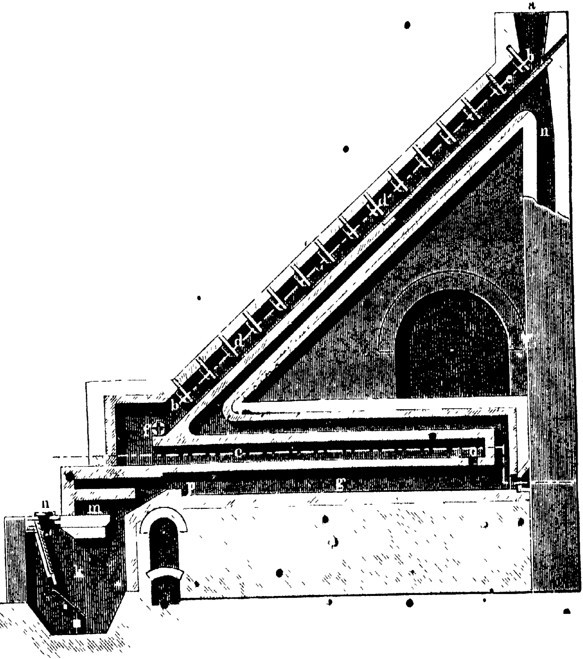


FIG. 129.

ore was pushed down into the furnace *g*, where it was burned completely by the fire from the gas-producer *k*. The sulphur dioxide formed here is certainly lost, and it constituted no inconsiderable portion (generally more than one-third) of the whole; but that formed in the muffle and on the inclined plane is strong enough to be carried into lead chambers and converted into sulphuric acid, certainly at no great profit, if any.

A large number of Hasenclever furnaces were erected on the Rhine and in Silesia, but they were found to utilise on an average only 60 per cent. of the sulphur as sulphuric acid. The remaining 40 per cent. SO_2, being mixed with the fire-gases, still escaped into the atmosphere, and were blamed for even more damage than they actually caused, the part played by the numerous zinc-works, glass-works, etc., being generally overlooked by the public (*cf.* p 113). We shall return to this subject in the seventh section of this chapter.

All these furnaces have become obsolete by the construction of blende-roasting furnaces, *which permit of utilising the whole of the sulphur of the ore in vitriol-chambers*, and thus do away with the extremely troublesome processes for absorbing SO_2, from fire-gases. All these modern furnaces have one principle in common: they combine the heat produced by the burning of the blende sulphur with heat applied externally, but in such manner that the fire-gases are kept entirely separate from the roasting-gases. It has been found that this indirect heat suffices for completely roasting the blende.

The furnaces which first realised the principle of utilising all the sulphur of the blende in vitriol-making, by completing the roasting by means of indirect fire, were invented by Max Liebig, who had the idea of constructing a sort of shelf-burner with shelves partially hollow and heated by indirect fire. His invention (Ger. P. 21032 of Eichhorn and Liebig) is described and illustrated (from the patent specification) in our second edition, pp. 273-275. *Cf.* also Eichhorn's report in *Fischer's Jahresber.*, 1889, p. 332.

We omit the description of the original style of these furnaces in favour of a modification known as "Rhenania furnaces," because they were constructed at the Rhenania Chemical Works at Stolberg (managed by R Hasenclever). These are now widely used, not merely for blende, but also for other poor sulphur-ores in the state of smalls or even of "peas" (pieces up to ¼-in. diameter), and for metallurgical products (matte) of the same kind.

The Rhenania furnace is shown in Figs. 130-133, in a shape in which it has been used for several years, and which embodies the same principle as the furnaces actually at work at present, which merely differ from the above in details, to be mentioned below. These furnaces require two men per shift, and roast about 4 tons blende per twenty-four hours, with a

and roast about 4 tons blende per twenty-four hours, with a consumption of 16 cwt. of coal. The temperature of the top muffle is 580° to 690°, that of the following muffles 750° to 900°. The progress of roasting is shown by the following percentages of sulphur:—

Raw ore	19·2	26·8	26·5
End of first muffle	17·6	19·1 to 21·9	15·9 to 21·4
" second "	12·0	11·2 " 14·3	9·9 " 12·4
" third "	3·4	1·02 " 1·48	0·75 " 1·66
" roasting	0·6	0·35 " 1·02	—

In the case of richer ores the second muffle does not require heating; the fire-gases may be conducted below the third muffle without a partition, and then at once over the second roasting-bed.

Jahne (*Z. angew. Chem*, 1894, p. 305) describes some experiments made with these furnaces. They are greatly improved by arranging a partition cutting vertically through all three muffles and thus dividing the furnace into two parts, without any change in the firing. This admits of roasting 30 per cent. more ore down to the same percentage of sulphur and saves labour. It is best to build two furnaces back to back. On the top beds the ore is spread in layers twice as thick as on the bottom beds, leaving small gaps between the charges, to prevent their getting mixed. It takes three or four days before a batch charged at the top is discharged at the bottom. The raking over and moving on of the batches, following upon the discharging of a finished batch, requires four hours. The most careful work must be bestowed upon the finishing of the batches in the hottest place; this lasts at best one and a half hours, usually three to four hours, sometimes seven to eight hours. Tests are made by adding hydrochloric acid to a sample, and looking for any evolution of H_2S. The sulphur can be brought down to 0·1 or 0·2 per cent.; it ought never to exceed 1 per cent., except in the case of blende containing limestone, which may retain 2 or 3 per cent. S in the shape of calcium sulphate. In regular work a charge of 9 to 12 cwt. roasted ore is drawn every six hours. One hundred parts of raw blende average 85 of roasted ore, and require 25 or 26 parts of good coal. The furnaces are provided with large dust-chambers, which must be cleaned every few weeks The dust consists mainly of zinc sulphate and calcium sulphate.

Lead oxide is carried farthest, even through the ten cylinders of a Hargreaves' plant connected with the furnace at Stolberg, right into the earthenware receivers of the acid-condensing plant. If the blende contains mercury, that metal is found in the mud of the vitriol-chambers connected with blende-furnaces, and can be recovered from it by distillation.

In *Chem. Ind.*, 1899, p. 25, Hasenclever gives some more details respecting the Rhenania blende-furnaces, which now roast 4700 kg. blende in twenty-four hours with two men per shift. Only for poor ores the fire plays round all the muffles; generally the ore is roasted in three superposed muffles and the fire plays only round the top and bottom muffle. Two furnaces are built back to back.' In order to avoid annoyance to the men, there is a space of 25 ft. between two opposite furnaces. Six furnaces are connected with one set of chambers, their flues being built closely together, to keep the heat, until they unite just in front of the Glover tower.

At Oker (1902) all "fines" of the ores used there passed through a 7 mm. sieve are roasted in Rhenania blende-furnaces. Each furnace roasts from 3·55 up to 5 tons ordinary ores or matte, according to whether the roasting is driven to 3 or to 7 per cent. S in the residue; and from 3 to 4·5 tons regulus, according to whether 2 or 6 per cent. S is left in the residue.

At Freiberg the Rhenania furnace is used (1902) for pyrites smalls and "peas" down to 5 mm. size (¼ in.) for blende, recently also for matte and speiss, containing about 20 per cent. S, 25 per cent. Cu, and 20 per cent. lead. For ores containing rather more sulphur the furnaces are provided with three muffles directly superposed. The fire-flue passes underneath the hearth of the bottom muffle, rises up at the end of this and along the ends of the second and the top muffle, and returns along the roofing-arch of the latter, so that the fire-gases heat only the bottom of the lowest and the top of the highest muffle. For poorer ores the furnaces have only two muffles, the fire-gases passing both under their top and over their bottom and between both muffles. With such furnaces, whether containing two or three muffles, the sulphur in the cinders from pyrites "fines" is brought down to 2 per cent., from pyrites "peas" to 3 per cent., from blende to 1 per cent., from matte and speiss to 5 per cent. Each furnace takes $3\frac{1}{2}$ to 4 tons ore per twenty-four hours, with a consumption of about 12 cwt. lignite and 6 cwt. coal; the work is done by two men per shift of twelve hours.

At Stolberg, in 1902, each furnace turned out 8 tons of roasted blende per day, with four men per shift, two on each side, and from 14 to 18 per cent. coal of the weight of roasted ore. The blende must be crushed to pass through a sieve of 2 mm. meshes. The product in the absence of lime shows 0·5 to 1 per cent. S, in the presence of lime correspondingly more. The roasting is stopped when a sample, treated with hydrochloric acid, does not stain lead paper. Sulphates (apart from calcium sulphate) are most easily formed when the furnaces do not go hot enough, *e.g.* after stopping for Sundays; once formed they are never completely decomposed.

Bémelmans (Ger. P. 76775) describes a furnace for roasting both pyrites and blende in separate compartments; the sulphur vapour obtained from pyrites, sometimes by addition of coal, is utilised for removing from the blende (which must not be mixed with coal) arsenic, antimony, and phosphorus in the shape of volatile sulphides.

Michel Perret (Ger. P. 37842) modified his well-known furnace for burning fuel in the shape of dust so as to roast blende, without mixing the fire-gases with the gases evolved by the burning blende. The principle is very similar to that of Eichhorn and Liebig.

Max Liebig (Ger. P. 237034) roasts blende or similar ores completely without any external heating of the furnace, by passing air, heated to about 1000° C., over the ore in spaces well protected against loss of heat.

Petersen (Ger. P. 196216) roasts blende in two furnaces, provided with a single fireplace, from which the gases first heat the lowest muffles of one of the furnaces, where the last stage of the roasting takes place, then the lower muffle of the second furnace, and only then they are divided into two streams for heating the higher muffles of both furnaces.

The Stolberg A. G., Borchers and Graumann (B. P. 24096 of 1906) heat a mixture of zinc-blende and finely divided metallic iron in an electric-resistance furnace, in which the charge forms the resistance, to 1000° to 1500°, in a continuous process Metallic zinc distils off and is condensed in the usual way; FeS remains behind in the molten state, is tapped off from time to time, then roasted, and the SO_2 given off is used for the manufacture of sulphuric acid.

Mechanical Blende-roasting Furnaces.

A furnace constructed by Zellweger and described in *Eng. and Min. J.*, 1900, p. 261, shows a roller-shaped stirrer. It turns out 30 tons in twenty-four hours.

Encke (Ger. P. 211433) describes a mechanical stirrer for blende-roasting furnaces of long shape, which saves much space and can be also applied to ordinary muffle furnaces.

The burner patented by J. Haas (Ger. P. 23080) is very similar to MacDougall's (*cf.* p. 474), but the single chambers, in lieu of having simple brick bottoms, are separated by flues through which pass the fire-gases from a coal-fire. Mechanical stirrers move the ore from the top shelf over three others and ultimately into an open hearth, where the last roasting takes place.

Hegeler's burner is a combination of an Eichhorn and Liebig's burner with a stirring arrangement somewhat similar to Spence's (p. 488), but differing from it in some important practical details. This furnace works most successfully at Mathiesen and Hegeler's zinc-works, La Salle, Ill. It treats 35 or 40 tons blende with 28 per cent. S in twenty-four hours.

Muhlhäuser (*Z. angew. Chem.*, 1910, p. 347) describes the evolution of this burner and its present sphere of application.

A mechanical blende-roasting furnace patented by the Chemische Fabrik Rhenania (Ger. P. 61043) has not been actually erected (*Chem. Ind.*, 1899, p. 26).

The burners patented by the Société Vieille Montagne (Ger. Ps. 24155 and 36609) are mechanical burners in which the flame of the coal-fire is not separated from the roasting-gases. These burners have been continuously at work at Oberhausen since 1883. Their construction is shown in Fig. 134. There are several superposed circular calcining-hearths, A, A, to which is attached a square calciner, B. The ground ore is charged through hopper *a* by means of feeding-rollers and flues on to the top chamber and gradually finds its way downwards and into B. The fire of the fuel burning on grate T first passes over B, then over the circular hearths A, A, into the dust-chamber C and into the flue S. The agitation is procured by the vertical shaft *b* and arms *e*, *e*, the stuffing-boxes being packed with asbestos. Shaft *b* is contained in an outer pipe *g*, and the air rising between them acts as a cooling medium. The arms carry tooth-rakes, *m*, in a radial position for the purpose of stirring, and slanting solid rakes, *f*, which move the ore from the circumference to the centre, or the other way, as is required for the purpose of gradually transporting the ore downwards and ultimately on to hearth B. [These furnaces, which had to be frequently repaired and made much flue-dust, are being gradually replaced by hand-worked muffle-furnaces, although according to Pierron (*Monit. Scient.*, 1900, p. 562) they consume only 18 parts coal for 100 blende.]

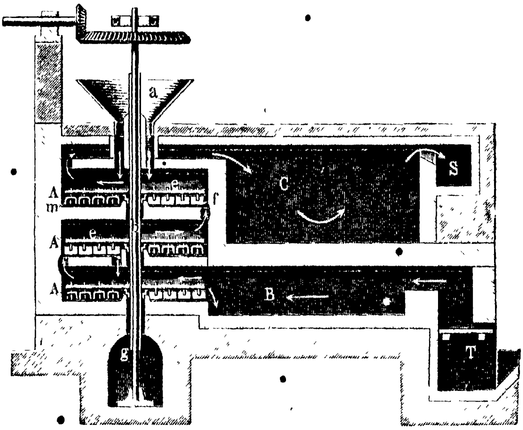


FIG. 134.

The O'Brien mechanical furnace (cf. *suprà*, p. 497) has also been adapted to the roasting of zinc-blende. It is for this purpose surrounded by a muffle, and is supplied with additional heat under three shelves, either by gaseous fuel, or by pulverised fuel, or from an outside combustion furnace. This furnace is shown in Fig. 135.

Trego (Amer. P. 398844) roasts blende in a furnace with revolving hearths.

Spirlet (Fr. P. 415338; Ger. P. 236089), employs for blende a succession of fixed and moving trays, the latter revolving on a vertical axis with stirring-blades, only the lowest tray is heated.

Schmieder (Ger. P. 244131) describes a revolving tube closed at both ends, with air-channels in the walls of the tube, where the air gets heated and issues into the zinc ore through holes protected by slanting pieces or by segment tubes against the entrance of ore dust.

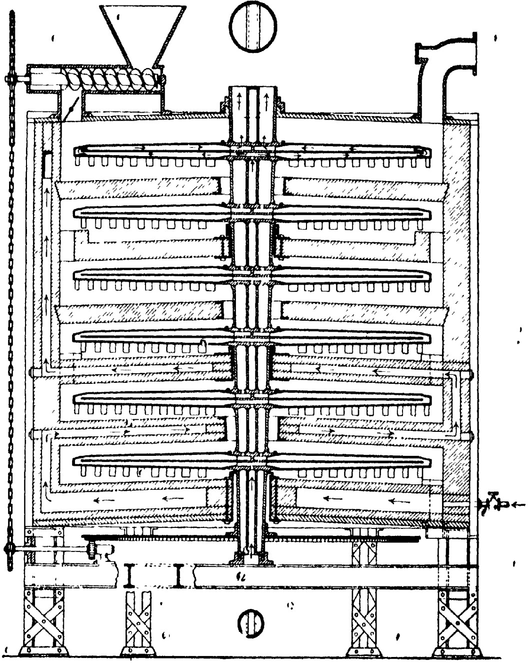


FIG. 135.

Schütz (*Chem. Zeit.*, 1912, p. 15) discusses the older blende-roasting furnaces and modern patents in the same line.

Olga Niedenführ (Ger. P. appl. N 10070) describes a mechanical roasting-furnace with special cooling-channels in the hottest spaces; on the top a covering of roasted ore in a granular form is spread, which at the same time serves as a filter for the dust.

Other blende-roasting furnaces are described in the B. P. 13625 (1909); 3843 and 3984 (1911), of Merton and Ridge.

Felix Thomas (*Chem. Zeit. Rep.*, 1910, p. 576) roasts blende at a low temperature in order to obtain zinc sulphate, and decomposes this by air containing much steam, according to the equation: $ZnSO_4 + H_2O = ZnO + H_2SO_4$. In order to produce steam and heat from within as well as from without, the roasted ore is made into briquettes with fuel. The decomposition of zinc sulphate in this case begins at 600° and is finished at about 820°; it can be therefore carried on with damp air at 100° lower than when working with dry air. He recommends briquetting the zinc ore with tar, pitch, caking-coal, etc., roasting the briquettes in the oxidising flame of a gas-producer at 700° to 750°, and in the end going up to 820°, preferably in revolving furnaces. This he expects to economise time, fuel, and loss of ZnO by volatilisation, to facilitate the application of mechanical roasting and to improve the result of roasting.

According to Hasenclever (*J. Soc. Chem. Ind.*, 1911, p. 1291) there is very slow progress in Germany for roasting zinc-blende by mechanical furnaces. Many German zinc-works have spent large sums of money on experimental furnaces of their own construction. The main difficulty in that respect seems to be the fact that most of the zinc-works are obliged to work with blende containing some lead, which ores sinter on roasting, and stick to the rods and moving parts.

Rules for Roasting Blende and similar Poor Ores, and for Treating the Cinders.—Hassreidter (*Z. angew. Chem.*, 1906, p. 522) maintains that roasted blende should contain as little sulphur as possible in the shape of zinc sulphide and sulphate, whilst other sulphates have no injurious action in the utilisation of the cinders. His analytical method for the estimation of zinc sulphide and sulphur has been mentioned, *suprà*, p. 112.

Doeltz and Graumann (*Chem. Centr.*, 1907, I. 1467) made an investigation on the decomposition and formation of $ZnSO_4$ during the roasting of blende.

Prost (*Bull. Soc. Chim. Belg.*, 1911, p. 103) proves that in the cinders from blende containing lime the sulphur is in the state of calcium sulphate, not in that of zinc sulphate.

Juretzka (Ger. P. appl. J 12275) makes the sulphates, contained in cinders from blende, harmless, for the subsequen distillation process by mixing them with dry lime and covering with water. The roasting-process remains in the usual form, and the whole of the sulphide-sulphur is obtained as sulphuric acid. The calcium sulphate is left in the cinders without interfering with the distilling-process for zinc.

Pape (Ger. P. appl. P26589) removes the sulphur from zinc sulphate by adding zinc oxide before the ignition. Thereby the SO_2 is split off on ignition completely and at comparatively low temperatures.

Jensch (*Z. angew. Chem.* 1894, p. 50) shows by analyses that the sulphur in roasted blende is contained therein mostly in the state of iron sulphide; already when roasting down to 2 per cent. S there is no more ZnS in the cinders. It is therefore unnecessary to carry the roasting down to 0·5 per cent. S in the cinders, as is frequently demanded.

Nemes (Fr. P. 426851) blows finely powdered pyrites, blende, etc., into a furnace where they slide downwards on an inclined plane. The hot roasting-gases travel underneath that plane. For roasting blende a special heating-contrivance is provided.

Hubner (Ger. P. 236669) roasts blende in a vacuum in several superposed chambers.

Treatment of Complex Ores containing Blende, Copper Ores, and of Other Ores yielding Poor Gases.—Hart (*J. Soc. Chem. Ind.*, 1895, p. 544) proposes treating such ores with sulphuric acid in a salt-cake pot, and when the mass has become pasty, transferring it to a blind roaster and finishing it there, all the gases going into vitriol-chambers. The zinc remains behind as sulphate, which can be obtained by lixiviation and crystallisation; or else it is mixed with poor zinc-ore and roasted, in which case the oxygen of the sulphate combines with the sulphur of the blende. The reaction seems to be:

$$ZnS + 4SO_3 = ZnSO_4 + 4SO_2.$$

The Maschinenbauanstalt Humboldt (Ger. P. 169694) treats ores composed of pyrites and blende as follows:—The ore is at first but slightly roasted, so that on the surface the FeS_2 is converted into FeS. It then passes a magnetic separator, and after leaving this, FeS and ZnS, now separated, are roasted in separate furnaces. Here FeS is completely roasted, and the gases, which are superheated and contain SO_2, are passed into the furnace where the ZnS is completely roasted, employing sc much air that the gases leaving this furnace can be employed for the superficial roasting of FeS_2 mentioned in the beginning; hence there is no fuel required for this, and the gases passing out of the first furnace contain all the sulphur of the ore as SO_2 in such concentration that it can be advantageously worked up. Another patent of this firm (Ger. P. 161154) treats of the case of ores containing but little pyrites, not sufficient for yielding enough heat on burning to roast the blende. This drawback is remedied by mixing such ores with enough fresh pyrites to yield sufficient heat on roasting for the roasting of the blende.

In order to enrich the SO_2 gases from ores not yielding sufficiently good gases, J. G. Jones (Amer. P. 872822) burns raw brimstone in a horizontal furnace and passes the heated gases into a horizontal revolving furnace, in which the poor sulphur ores travel in the opposite direction; thus both sources of sulphur are utilised for producing gas rich in SO_2. The coke produced is continuously removed from the revolving furnace.

O. Niedenfuhr (Ger. P. appl. N10069) effects the simultaneous roasting of easily burning and more difficultly treated ores (only of pyrites and zinc-blende) by preventing the ores from getting mixed. On each shelf of the burner there is only one of this kind of ores, in turns; or one furnace is arranged inside the other, with special stirrers.

Channing and Falding (Amer. P. 962498) utilise the gases from the "*pyritic smelting*" *of copper ores*, which hitherto were wasted on account of the irregularity of their composition and the small percentage of SO_2 contained therein, in the following manner. The addition of coke in the fusing process is kept as low as possible, in order to avoid unnecessary dilution of the gases with CO_2 and N; say, 1 part coke to 4 parts of available sulphur in the sulphides. The air-blast is to be regulated in such manner that, after the oxidising processes have been accomplished, an excess of 4 or 5 per cent. C remains in the gases. In order to keep the percentage of SO_2 in the roasting-gases between 5 and 8 per cent., as is the rule both for the chamber- and the contact-process, and to obtain gases of uniform quality, they are conducted from the single furnaces into a large mixing chamber; if they are too rich in SO_2, air is introduced in some suitable place; if too poor, some of the furnaces are charged with richer ore.

Reverberatory furnaces applicable to the production of blister copper, together with SO_2 in a state in which it can be used in vitriol chambers, are described by T. Walker in B. P. 9918 of 1909.

The recovery of sulphur trioxide and sulphuric acid from the gases of "pyritic" copper smelting, containing 3½ per cent. SO_2 is described in detail by Freeland and Renwick (*Eng. and Min. J.*, 1910, pp. 1116-1120). This is done by the Ducktown Sulphur, Copper, and Iron Co. in Tennessee to the extent of 160 tons acid of 60° Bé. per diem.

Carmichael (Ger. P. 175436) roasts ores and metallurgical products containing sulphides in a converter, with addition of calcium sulphate or sulphide, in such manner as to obtain, on one side, the metals as such, and, on the other side, gases rich enough in SO_2 to be worked for sulphuric acid.

Sweeting (Fr. P. 361808) utilises the SO_2 given up in the roasting of *antimony ores* by absorbing them in water; the antimony oxide carried along with the gases is filtered or decanted off.

The furnaces or kilns for roasting ordinary copper-ores, lead-ores, and so forth, as far as they are not mentioned in previous places, cannot be described in this book, as they belong to the domain of metallurgy proper, and in these cases the roasting-gases are, if at all, sent into vitriol-chambers merely to get rid of them, but without the expectation of profitable work.

We merely mention a few modern attempts to obtain workable roasting-gases from such ores by new methods.

Sébillot (B. P. of 21616 1898) charges cuprous or other sulphur-ores, mixed with fuel, into a furnace provided with air-blast. The gases are taken into a chamber containing coke, pumice, or a suitable metallic oxide, where they are treated with air and steam, and where sulphuric acid is formed (*cf.* Chapter IX.).

The ordinary *lead ores* smelted in Europe contain but 11 to 15 per cent. sulphur, and by the old roasting processes yield burner gases containing about 1 per cent. of sulphur which are, of course, quite useless for the manufacture of sulphuric acid. Richer gases are obtained by the process of Huntington and Heberlein (*B. P.* 8064 of 1896; 3795 of 189[illegible]) in which air is blown in a "converter" through a layer of lead ore 3 ft. deep.

In the beginning and at the end of the roasting, gases very poor in SO_2 are obtained; but during the most active stage the gases contain up to 15 per cent. SO_2, and by working a large number of converters charged at different times, a fairly continuous gas current can be obtained, which is sufficiently rich in SO_2 for conversion into sulphuric acid. According to Hasenclever (*J. Soc. Chem. Ind.*, 1911, p. 1291), the manufacture of sulphuric acid by that process was first introduced at the Muldenhütte at Frieberg, Winkler's contact process being used; at the Friedrichshutte at Tarnowitz in Silesia the roaster gases are treated by the chamber process.

While the Huntington-Heberlein converters work intermittently, the work of the Dwight-Lloyd furnace, improved by Schlippenbach, is continuous. In this apparatus (mentioned by Hasenclever, *loc. cit.*) the air is not blown through the material from underneath, but sucked down across it from the top to the bottom. This furnace delivers a regular gas-current of 4 to 6 per cent. SO_2 by separating continuously the rich from the poor gases. Probably about 90 per cent. of the sulphur of the lead sulphide can be utilised for the manufacture of sulphuric acid, so that 4 tons of lead ore will yield 1 ton of sulphuric acid of 142° Tw. A large plant for the manufacture of sulphuric acid by the contact process combined with furnaces of this design was in the course of erection at Stolberg in October 1911, and was to be started in a few months. Some difficulties are certainly anticipated for the beginning, as the gases contain 5 or 6 per cent. CO_2 and much dust.

If all the lead ores smelted in Germany were to be treated in this way, they would yield about 40,000 tons sulphuric acid of 142° Tw. *per annum*. The production of acid from this source in England would be about 6000 tons; in Belgium, 18,000 tons; in France, 12,000 tons; in Spain, 75,000 tons.

D. THE PRODUCTION OF SULPHUR DIOXIDE FROM VARIOUS OTHER MATERIALS.

1. *Burners for the Spent Oxide of Gas-works.*

The spent oxide of gas-works is now generally washed, so as to obtain ammonia salts therefrom, and is also frequently treated for the ferrocyanide or sulphocyanide. At all events the sulphur, which it contains in the free state, sometimes up to 50 per cent., is ultimately burnt for the manufacture of sulphuric acid. This is sometimes done in ordinary brimstone-burners, as shown *suprà*, pp. 391 *et seq.*; but in this case it is difficult to burn it out completely, and there is loss of sulphur in the cinders. Ordinarily it is burnt in apparatus very similar to "shelf-burners," as shown in Fig. 136 (Hill's burner). Each chamber in this case is about 10 ft. long, 20 in. wide, and 9 in. high. MacDougall's and Herreshoff's mechanical burners (pp. 474 and 482) have also been employed for this purpose.

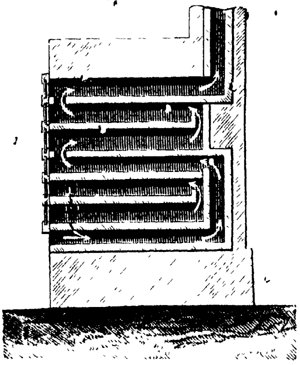


FIG. 136.

Cowen's burner, Figs. 137 and 138, consists of a row of fire-clay gas-retorts, and requires no further explanation. Other works are said to burn that material in burners with very narrowly placed grate-bars.

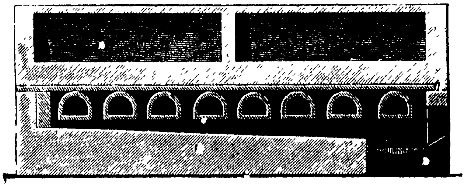


FIG. 137.

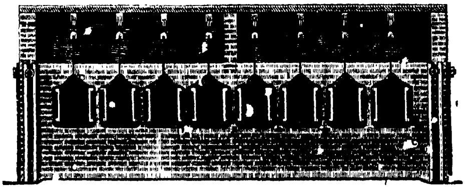


FIG. 138.

Sometimes the oxide is moulded into bricks and put into lump-burners; it burns off very well and the cinders fall through the grate-bars by themselves; in fact, the bars must be touched as little as possible. This process does not answer so well as shelf-burners.

The 38*th Alkali Report*, p. 97, recommends not to discharge the hot residue from oxide burners through the front working-doors, as this causes a nuisance, but to push it into chambers placed at the back, where they can cool off. The gases should be taken through long, heated flues, in order to burn the tarry substances and ammonia which destroy nitre.

2. *Burners for Sulphuretted Hydrogen.*

These are usually of a very simple description. Those shown in Fig. 139 consist of a brick chamber provided with

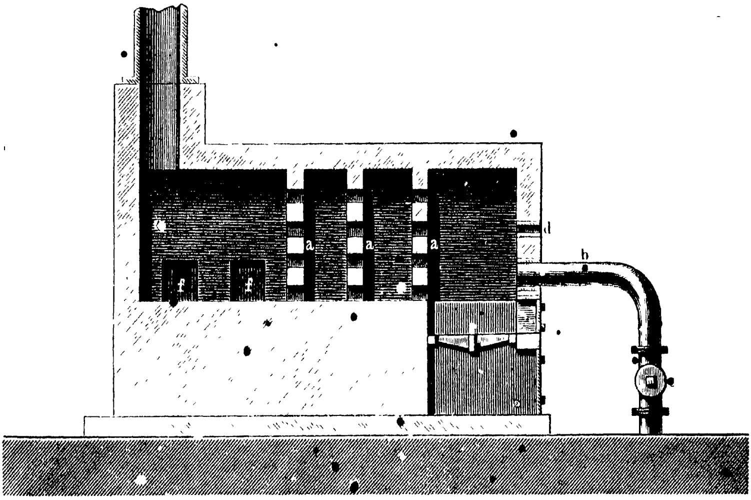


FIG. 139.

some baffling-walls *a*, *a*. The sulphuretted hydrogen gas (which is nearly always mixed with a large quantity of inert gas, chiefly nitrogen) is introduced through the cast-iron pipe *b*, the supply being regulated by an inlet-valve *c*. Air is admitted partly round the pipe *b*, partly by a special opening *d*, which ought to be provided with a slide or other means of regulating the amount of air. The heat produced by the combustion of the sulphuretted hydrogen is quite sufficient for keeping the temperature of the chamber at a red heat, so that the gas is always lighted again if by chance the flame has been extinguished. This is aided by the baffling-walls, *a, a,* which serve both the purpose of supplying a reservoir of heat for the just-mentioned purpose, and of mixing the gases so as to ensure perfect combustion. The grate, *e*, is required only for irregularly composed gases, like those formed in the saturation of the gas from ammonia-stills by sulphuric acid; especially for relighting the gas after stoppages over Sundays, and so forth. With gases of regular composition and comparatively rich in sulphuretted hydrogen, like those given off in Chance's sulphur-recovering process, the grate *e* is quite unnecessary, as these gases are as easily lighted and kept burning as coal-gas The doors *f, f* serve for "potting" the nitre, where it is not preferred to employ more rationally constructed apparatus for this purpose (*cf.* Chapter V.) The size of the whole chamber may be about 10 to 12 ft. long, 4 or 5 ft. wide, and 3 ft. high. Pans for concentrating sulphuric acid may be placed upon it, and even in this case the gases will issue hot enough to do full work in a Glover tower. Sublimation of sulphur is never observed with ordinary care in admitting the air. One very great advantage in burning sulphuretted hydrogen is this: that, in contrast with the variations in the amount of SO_2 in burning brimstone or pyrites, even when keeping up a regular rotation of the burners, the process in this case is perfectly continuous, as the supply of H_2S from the gas-holder is continuous; the amount of air need never be varied when once regulated; the percentage of SO_2 in the burner-gas is altogether uniform; the chamber process is consequently much more regular than with brimstone or pyrites, and the consumption of nitre is correspondingly smaller. All this, however, holds good only if the percentage of H_2S in the gas is practically constant, whilst with gases of very varying composition, such as those evolved in ammonia-works, the very contrary is the case.

It must be remarked that at some works, in burning the sulphuretted hydrogen from the Chance process, an increased consumption of nitre has been noticed, whilst at others a saving in nitre in comparison with the burning of pyrites has been effected. Evidently in the former case the quality of the sulphuretted hydrogen has not been, as it ought to be; it has no doubt varied in percentage, and may even have contained a notable quantity of carbon dioxide, so that the chamber-process would not be as regular as desirable. Sometimes it has been noticed that the combustion has not been quite perfect, so that sublimed sulphur has been found in the Glover tower or even in the chambers; but this is evidently owing to mistakes and careless work, and should not occur with ordinary care.

In 1886 E. Lombard (*Monit. Scient.*, 1889, p. 1231) described a shelf-burner for sulphuretted hydrogen, consisting of two separate compartments, 7 ft. 6 in. deep inside. There are four shelves, 6 ft. 6 in. long and 1 ft. 4 in. wide, formed of four fireclay slabs each. The top shelf is perforated with many holes, and occupies the whole length and width of the furnace; the other shelves are not perforated, and leave at alternate ends a passage of 12 × 16 in. for the gases. Each furnace is provided at the base with four burners for H_2S and two air-tubes, disposed in two tiers of three each, the air-tubes occupying the central places. The burners consist of fire-clay tubes, 6 ft. 6 in long, $1\frac{1}{2}$ in. wide inside, and $\frac{3}{8}$ in. thick, projecting two-thirds of their length into the furnace, and provided on the top with slits or holes for dividing the gas. They are connected in front by a cast-iron tube with a stop-cock for regulating the flow. The air-tube is $2\frac{1}{2}$ in. wide, and is provided with an iron thimble for regulating the quantity entering. The gaseous products of combustion pass into a flue, 1 ft. 6 in. × 2 ft., on the top of the furnace, then into a small dust-chamber, and then into the Glover tower. Total height 6 ft. The pressure of the gas is $= 1\frac{1}{2}$ in. of water; it is said to work very well.

Simpson and Parnell (B. P. 14781 of 1886) regulate the supply of air and gas in any desired proportion, so as to obtain either free S or SO_2, by employing two vessels, each of which is provided with an inlet and an outlet valve. Both vessels are filled and emptied simultaneously by a mechanical arrangement, the two vessels acting in conjunction, so that the gas entering and leaving one of the vessels bears a constant proportion to the quantity of air entering and leaving the other vessel. [Such an arrangement, very useful as it undoubtedly is for the production of free sulphur from H_2S, seems unnecessarily complicated when the object is that of burning the H_2S with an excess of air for the purpose of sulphuric-acid manufacture.]

Barth (Ger. P. 235157) converts the H_2S contained in the gases evolved from gas-liquor by burning into SO_2, and mixes the combustion products again with the first gases, before they are carried further into the apparatus for retaining the NH_3 in the shape of ammonium sulphate.

3. *Processes for Absorbing Sulphur Dioxide contained in Acid-smoke, Fire-gases, and the Like.*

The abatement of the nuisance caused by the acid-smoke given off in metallurgical and other operations presents special difficulties where the percentage of acids is so slight that their utilisation by condensation or by conversion into sulphuric acid is out of the question; that is, if less than 4 per cent. SO_2 by volume is present. The damage done by such acid gases has been described in Chapter III., pp. 269 *et seq.*

A survey of the processes tried a number of years ago at Stolberg for dealing with acid-smoke has been given by Hasenclever (*Fischer's Jahresber.*, 1881, p. 173). All of these will be mentioned below; they all have one common feature: they are very expensive, and at the same time they hardly ever attain their purpose completely.

The problem of dealing with the enormous quantity of sulphur dioxide contained in *ordinary coal-smoke* has been hardly ever attacked in a serious manner, as the expense and inconvenience of any imaginable measures for this purpose have hitherto appeared to be quite unbearable; and it does not seem as if this would be different in the near future. The only practicable remedy in this case, as well as in some cases of metallurgical smoke, is to dilute the gases with a large quantity of air, by erecting very tall chimneys for carrying them up to a considerable height above the surface of the earth. Such chimneys have been made up to 450 ft. in height. In the case of hydrochloric acid they have entirely failed in their object (*cf.* Vol. II.), but in that of sulphur dioxide the dilution of air is more efficient. Freytag certainly estimates (somewhat arbitrarily) that smoke is harmless only when it does not contain beyond 0·003 per cent. SO_2 by volume; but since, for instance, in lead-works the percentage of SO_2 in the main flues, where all the smoke and fire-gases are mixed, rarely exceeds 0·1 per cent., it is very likely that, if these gases are allowed to escape only 200 ft. or more above any vegetation, they get sufficiently diluted with air in their descent to become harmless. This is owing to the fact that sulphur dioxide diffuses pretty equally in the air, whilst hydrochloric acid, sulphuric anhydride, acid salts, etc., which form visible fumes, generally reach the ground in a very little-divided stream, and cannot therefore be made innocuous by very tall chimney-shafts. In fact, this is the only explanation why the scores of tons of sulphur dioxide daily belched forth in certain localities by lead-works, zinc-works, glass-works, etc., have not ere now destroyed all vegetable life around the works, which is notoriously the case only in a few isolated instances. But as such instances do occur, and as altogether the requirements of sanitary authorities are constantly becoming stricter, the removal of the acid-smoke to a high level by means of chimneys cannot be pronounced a final solution of the difficulty, even where only SO_2 is the acid concerned, all the more as in moist weather the acids escaping from the very tallest chimneys are brought down to the ground in a somewhat concentrated state.

A proposal has been made by Wislicenus and Isachsen (Ger. P. 124900) to dilute smoke-gases to such an extent that the amount of acid contained in them becomes innocuous. This is to be attained by building within the chimney-stack a second lower stack, provided with pipes carried up and downwards. Air is introduced into the inner stack and escapes partly at its top, partly through the up and down pipes, thus intimately mixing it with the chimney gases. [It is not likely that this process can be carried out in many cases as prescribed above, but it is stated in the 38*th Alkali Report*, p. 76, that bringing down the percentage of acids in the exit gases from chemical works by means of diluting them in the chimney with air is not contrary to the law.]

O. Schott (*Dingl. polyt. J.*, ccxxi., p. 142) proposed *to utilise the sulphur dioxide given off in making glass from sodium sulphate for the manufacture of sulphuric acid*. The gas is to be made richer in sulphur by employing for the glass-mixture gypsum in lieu of limestone. Sulphate of soda, gypsum, and coal are to be mixed in proper proportions, and brought to a bright red heat in muffle-furnaces or in elliptical glass pots, until the SO_2 is driven off. The fritted residue of sodium and calcium silicate is to be powdered and used by glass-works; the gas is to be conducted into lead chambers and worked for sulphuric acid. This process seems entirely impracticable; especially since such diluted gas (mixed with a great deal of carbon dioxide) has not yet been utilised.

Thirion (Fr. P. 28th February 1874; Wagner's *Jahresber.*, 1875, p. 391) makes a similar proposal for heating sodium sulphate with coal and silica, whereby a mixture of sulphur vapour, sulphur dioxide, and carbon monoxide is cooled. The sodium silicate is to be decomposed by CO_2 or to be used as such. [As a proposal for manufacturing sulphur or sulphuric acid this process is evidently hopeless.]

We will now give a synopsis of the various methods for treating ordinary acid-smoke, with special reference to the removal of SO_2 and SO_3. For details we must refer to the sources quoted in this work, to a special treatise by C. A. Hering, *Die Verdichtung des Huttenrauches* (Stuttgart, 1888), and to one by Schnabel, *Metallhuttenkunde*, ii. pp. 58 *et seq.*

Condensing by water seems to be the simplest and most obvious process, looking at the great solubility of sulphurous and sulphuric acid in water. But this process is in reality only practicable where the percentage of acids is not too slight; dilute acid-smoke cannot be sufficiently washed without employing a comparatively enormous quantity of water; and, surprising as it is, SO_3 is even more difficult to condense in this way than SO_2. It is quite certain that condensation by water can be made to *pay* only where the gases are sufficiently concentrated to convert them into sulphuric acid in lead chambers; it is therefore the interest of smelting-works, etc., to conduct their processes in such a manner that the acids are diluted with as little inert gases as possible. If the percentage of SO_2 reaches 4 per cent. by volume, they may be submitted to the Schroeder and Haenisch process (*vide infrà*), or they may even be converted into sulphuric acid, although this will hardly leave any profit at that percentage; but it is enough to have removed the nuisance. Where, however, there is less than 4 per cent. of SO_2 in the gases, any *utilisation* is out of the question; the thin acid liquids obtained by washing the smoke must be run to waste (which in most cases means a fresh nuisance, and is not permitted by the authorities); nor is the SO_2 and SO_3 anything like completely taken out of the gases; and the nuisance is at best only diminished, but not remedied.

At all events the contact of the absorbing-water with the acid gases must be made as intimate as possible. The condensing-apparatus used for hydrochloric acid, and described in Vol. II., are suitable only for somewhat strong gases; the weak gases which we are here treating of require special means, such as paddle-wheels or similar spray-producing apparatus, costly to work and to keep in repair, and generally imperfect in their action.

Haworth (Amer. P. 268793 of 1882) proposed to condense the SO_2 given off in lead-smelting by water, boiling it out of the solution and taking it into a lead chamber—an economically hopeless process.

In lieu of water, Freytag (Ger. Ps. 9969, 14928, 15546) and Hasenclever (Ger. P. 17371) employ somewhat concentrated *sulphuric acid*, in an ordinary coke-tower of large size. This agent retains the sulphur trioxide much better than water, so that in some cases the expense of working the process is paid by the sulphuric acid recovered. Sulphur dioxide is also retained to some extent, but only if the gases have been well cooled. The necessity of doing this and of previously removing the flue-dust, which is sometimes very difficult to perform, is a great drawback to this, as well as to all corresponding processes. In fact Freytag's process has been abandoned again; at the best it could remove only a small portion of the injurious constituents from the acid-smoke. (Schroeder and Haenisch, *Chem. Ind.*, 1884, p. 118.)

Babé and Pape (Ger. P. 187381; B. P. 19973 of 1906) pass the gases, previously cooled and washed, through a second chamber, *cooled* down below 0°, *e.g.* by lumps of ice, or on the outside by the evaporation of liquid ammonia or sulphur dioxide. Here the aqueous vapour is condensed and retains all the SO_2 present in the form of a saturated solution. If necessary, a little more water is introduced, or else an aqueous solution of salts not decomposable by SO_2.

H. Howard (Amer. P. 889132) absorbs the SO_2 from dilute gas by water, drives it out by heating, cools the concentrated gas and absorbs it by a sulphite solution.

Borchers (*Chem. Centr.*, 1909, ii. p. 1177) obtains technically available solutions of SO_2 from dilute gases by repeated automatic supply of water or weak solutions of SO_2 to absorbing-towers.

Drewsen (Amer. P. 981625) utilises gases poor in SO_2 by absorbing this in water, and driving it out of the solution by the heat of the burner gases

Edmunds (B. P. 8006 of 1910) describes an apparatus for this purpose.

Burbury (Fr. P. 420596 and additions) atomises water in apparatus for the absorption of SO_2, and injects it into the tube through which the gas is passing on its way from the furnace to the absorbing vessel.

Absorbing the acids by caustic lime, generally in the shape of a cream of lime, is one of the oldest and, if properly carried out, still one of the most efficient ways of removing the acid-smoke nuisance. Where the quantity of acids is but slight, and the manufacture in question is sufficiently profitable otherwise, this process is even now applicable, and if properly applied it does remove practically all the acids. The cream of lime should meet the gases in a finely divided state, either by flowing down properly constructed towers, or, still better, by being converted into a spray by means of paddle-wheels or the like (*cf.* Rayner and Crookes' patent, B. P. 1678 of 1875). That this leads to the desired effect, even with the large quantity of SO_2 emitted in roasting blende, has been proved by working on the large scale in Upper Silesia (*cf.* Bernoulli, *Fischer's Jahresber.*, 1880, p. 184). But unfortunately the expense of this process, where large volumes of acid gases are concerned, is very serious, more especially as nothing like the whole of the lime can be utilised for absorption, and the attempt to sell the product as bisulphite of lime (Hasenclever, Ger. P. 10710) has failed (*cf.* Schroeder and Haenisch, *Chem. Ind.*, 1884, p. 118).

According to Jensch (*Fischer's Jahresber.*, 1889, p. 321) the deposit forming in the milk of lime towers contains so much lime that it can be used over again, and at least a product is obtained containing 37·7 per cent. lime, 38·4 SO_2, 2·8 SO_3, 4·1 CO_2, etc., which is very useful as an addition to animal manure for the purpose of fixing the ammonia, in which respect it is equal to gypsum.

It has been found by Cl. Winkler and other observers that the SO_2 in smoke is much more injurious to vegetation if accompanied by much steam, *e.g.* in smoke-gases from brick-kilns. Spitta (Ger. P. 110388) proposes to absorb SO_2 and steam at the same time by passing the gases up and down several flues, into which slaked lime in the shape of dust is injected from the top. The bisulphite of lime formed is removed from the bottom of the flues by means of special doors.

Egestorff's Salzwerke (Ger. P. 70396) describe as a very efficient apparatus a series of chambers with inclined bottoms, connected with collecting-tanks. The alkaline absorbing liquid is pumped up over and over again and brought into contact with the gases by means of a spray producer.

Limestone is very much cheaper than caustic lime, and is almost equally efficient if employed in the proper way; that is, if a very large surface of limestone is exposed to the acid gases, and if this surface is kept from being covered with a crust of sulphite by being constantly washed with a stream of water. Cl. Winkler has constructed a special arrangement for this purpose (Ger. P. 7174) which completely fulfilled its object at the Schneeberg ultramarine works. It consists of three brick chambers filled with large pieces of limestone, the roof being formed by plank covers perforated with many holes, through which water is kept running on to the limestone. The gases pass through these chambers successively and in regular rotation. The absorption of SO_2 is excellent, but as each cwt. of sulphur requires 3 cwt. of limestone, it is still too dear for most metallurgical purposes, especially as any utilisation of the sulphur is out of the question.

The limestone treatment is frequently employed at sulphate-of-ammonia works for getting rid of the SO_2 formed by combustion of the H_2S escaping from the saturators. This treatment is frequently mentioned in the Alkali Inspectors' Reports, and in the 36*th Report* (for 1899), pp. 25 and 26, Mr R. Forbes Carpenter, the Chief Inspector, states the following conditions as being absolutely necessary for success:—1st. There must be sufficient draught at the furnace, and the suction at the condenser outlet must be adequate to supply this at all times to avoid sublimation of sulphur. Such draught might be supplied by injecting air under slight pressure in the furnaces. 2nd. The gases must be completely cooled before and behind the furnace. If they enter the limestone-tower above 38° C., much calcium sulphate is produced, which forms a protective crust on the limestone. The hot gases are to be cooled first by cast-iron pipes until some condensation takes place, when leaden pipes must be substituted for them. 3rd. The limestone-tower should be made of wood planks, tongued and grooved, or of brick and cement, not of cast iron. [The latter material would surely not be dreamt of by a chemical engineer in such a case, but possibly it has been used in gas-works!] 4th. The supply of water is best made in two forms, one constant, the other intermittent (by flushes), especially in the case of limestone, but with hard chalk the intermittent flush only may be used, at not too long intervals. [*Cf.* the much better feeding methods for Gay-Lussac and Glover towers described in Chapter VI.]

Precht (B. P. 3443 of 1881) employs for absorbing SO_2 from gaseous mixtures either *magnesium hydrate* or *aluminium hydrate*, especially the former. It is either spread upon trays moistened with water, or is brought into contact with the gases (previously cooled to 100°) in the state of a cream, in an apparatus provided with a mechanical agitator, or in columns like those employed for treating sulphuric acid by sulphuretted hydrogen (Chapter X.). This produces a crystalline precipitate of magnesium sulphite, besides a solution of magnesium sulphate. On heating the magnesium sulphate to upwards of 200° the SO_2 is split off, and can be condensed as such or converted into sulphuric acid, whilst magnesia remains behind, together with about 3 per cent. magnesium sulphate. The latter is heated with coals, and thereby converted into MgO, remaining behind, and a mixture of SO_2 and CO_2, which is utilised in vitriol-chambers [that will be hardly possible!]. M. Lyte (*J. Soc. Chem. Ind.*, 1882, p. 165) gives a detailed description of this process, with diagrams. It has been tried at several places, but has evidently been found too little advantageous for most purposes.

Alumina is included in Precht's patent, but is less efficient than magnesia. Sometimes acid gases have been passed through layers of clay-slate (schist), whereby sulphate of alumina has been formed, but this process is evidently only practicable under special local circumstances.

Zinc carbonate or *oxide* was proposed by Schnabel (*Fischer's Jahresber.*, 1882, p. 266), who had previously made manifold attempts at the Lautenthal smelting-works for treating the acid-smoke, all without any sufficient success. Ultimately a process was adopted (Ger. P. 16860), consisting in passing the gases over basic zinc carbonate moistened with water. Zinc sulphate is formed, which, on heating (preferably mixed with coal), yields sulphur dioxide, to be converted into sulphuric acid in lead chambers, and a porous residue, consisting of a mixture of zinc oxide with basic zinc sulphate. Schnabel's apparatus is rather complicated, and the result not very satisfactory; the process is very troublesome to carry on, and costs much more than the value of the sulphuric acid obtained (a provisional protection, 5416 of 1881, for this process was taken out in England by M. Lyte).

Fleischmann (Ger. P. 17397) passes the sulphurous gases, together with some air, through a kiln containing a mixture of *ferric oxide* and coal. The latter, in burning, yields the necessary heat, and at the same time reduces the Fe_2O_3 and SO_2, so that FeS collects at the bottom.

In Saltlake City the SO_2 contained in the smoke of the copper-works is retained by the bases of scoria blown into a kind of glass-wool.

Metallic iron, moistened by water, was employed by Winkler (Ger. P. 14425), but was not found practicable for dilute acid gases. Thorp (B. P. 8862 of 1889) again recommends towers filled with scrap-iron, and kept moist with water or a solution of ferrous sulphate, the temperature being maintained at from 49° to 71° C.

Metallic copper or *zinc*, in very finely divided form, was tried at the Frankfort Scheideanstalt, but without sufficient success; but at the same works the following interesting process was worked out.

Rössler (*Dingl. polyt. J.*, ccxlii. p. 278; *Fischer's Jahresber.*, 1881, p. 184) showed that gaseous mixtures, containing, besides a large excess of air, far too little SO_2 and SO_3 for being treated in vitriol-chambers and otherwise not treatable in any efficient manner, can be completely deprived of both the above acids by forcing the gases, by means of a Körting's injector and a perforated coil of pipes, *below the surface of water*, holding some *copper* in suspension or some *cupric salt* in solution. The cupric sulphate acts as a carrier of the oxygen of the air upon the SO_2, and large quantities of sulphuric acid are formed in this way, so that this process might even be employed for manufacturing sulphuric acid. At Frankfort, however, it was carried out in this way, that the tank into which the gases are passed is always supplied with precipitated copper, from which by this process cupric sulphate is obtained without any expense. Rössler has also applied this principle to the treatment of ordinary acid-smoke (Ger. P. 22850), by combining a whole set of apparatus. This process is very adversely criticised by Friese (*Chem. Ind.*, 1895, p. 137), who has made a long series of experiments with it, with totally negative result. No oxidation of SO_2 with air to SO_3 by the catalytic action of $CuSO_4$ could be proved. SO_2 reduces a hot solution of $CuSO_4$, with intermediary formation of cupric sulphite, to metallic copper. A smooth and easy oxidation of the cupric sulphite to sulphate does not take place. Hence this process would be useless for the production of cupric sulphate, and still more so for that of sulphuric acid.

A special class of processes utilises the reaction between *sulphur dioxide* and *hydrogen sulphide*, either both being in the state of gases, or the latter being in the nascent state as evolved from sulphides. The reaction in its simplest form is:

$$2H_2S + SO_2 = 2H_2O + 3S;$$

but, apart from the fact that polythionic acids are formed by secondary reactions, the above reaction is anything but complete in the case of very dilute gases. Details about it are given in our Vol. II, pp. 967 *et seq.*, edition of 1909, in the chapter treating of the recovery of sulphur from soda-waste; in this place it may suffice to mention that a patent founded upon the above reaction was taken out by Landsberg (Ger. P. 6364) in connection with the roasting of blende.

When sulphides are employed, the reactions are even more complicated, but the absorption of SO_2 can be made more complete. Cl. Winkler (*Fischer's Jahresber.*, 1880, p. 245; more details in *Chem. Ind.*, 1880, p. 126) described a very interesting process for dealing with the gases from an ultramarine works containing much SO_2. They were brought into contact with a solution of *sodium sulphide*, obtained from the sulphate going to waste in that manufacture, by reducing it with coal. The SO_2 is completely absorbed, with formation of sodium thiosulphate, or, in another modification, with formation of free sulphur; but on the large scale sodium tetrathionate was formed, which had to be decomposed by heating into sodium sulphate, SO_2, and free sulphur. *Theoretically* nothing was consumed but coal, but evidently a very large amount of fuel must have been used in the various evaporations and furnace operations, with an amount of skilled labour out of proportion to the value of the products obtained. After having been carried out from 1868 to 1877, the process just described was abandoned for a simple absorption by limestone moistened with water (p. 525). Even before Winkler, in 1864, Jacob had carried out for some years a similar process to that just described, employing either sodium or calcium sulphide, at Munsterbusch (*Fischer's Jahresber.*, 1881, p. 181).

Calcium sulphide, proposed many years ago by Dumas, forms also the absorbing substance in Kosmann's process (Ger. P. 13123). By reducing calcium sulphate with coal and lixiviating, a solution of calcium sulphydrate is obtained, which in very finely divided state is brought into contact with the gases containing SO_2. The result is the formation of sulphur and gypsum:

$$5SO_2 + 2CaH_2S_2 + 2H_2O = 7S + 2CaSO_4, 2H_2O.$$

The sulphur is extracted from the mixture by superheated steam, and the gypsum returns into the cycle of operations [it is very doubtful whether this would succeed!]. From further communications by Kosmann (*Fischer's Jahresber.*, 1882, p. 270), it appears that the absorbing medium was afterwards prepared by boiling sulphur with milk of lime, that is, as the ordinary "liver of sulphur," and that the whole process was entirely in the experimental stage (from which it does not seem to have emerged).

Barium sulphide, which was experimentally tried at Freiberg, proved much too costly.

Vegetable charcoal was proposed by A. H. Allen (B. P. 189 of

1879), who passes the gases, freed from dust, through drying-towers fed with sulphuric acid and then through columns filled with charcoal, previously ignited in a stream of nitrogen, where the SO_2 is retained, whilst the nitrogen passes on. By a vacuum or by heating to 300° to 400°, or by a combination of both, the SO_2 is to be driven out and utilised. (This process, apart from the prohibitory expense, is hardly practicable, because the gases in question contain nearly always a large quantity of oxygen which will convert the SO_2 to a great extent into sulphuric acid within the pores of the charcoal.)

A totally different way of employing coal is used in one of the oldest processes for dealing with acid-smoke, namely, *passing the gases through red-hot coals*, in order to reduce the SO_2 to sulphur. This has already been mentioned in Vivian's pamphlet, "Proceedings of the Subscribers to the Fund for obviating the inconvenience arising from the Smoke produced by smelting Copper Ores" (London, 1833), and in a pamphlet by Reich, describing the experiments made at Frankfort in 1858, and it has been proposed over and over again, with the same negative results. A new apparatus, by Schroeder and Haenisch (Ger. P. 33100), was said to give good results, nearly the whole of the SO_2 being reduced to S; but their process evidently works only with rich gases, and does not deal with those poor gases which concern us here.

Bémelmans (Ger. P. 77335) converts the SO_2 by reduction with carbon and hydrogen into H_2S, dries this by the process to be described below, mixes it with dry SO_2, and converts them into H_2O and SO_2.

4. *Various Processes for obtaining Sulphur Dioxide by Other Methods.*

From nitre-cake (acid sodium sulphate) Bottée (B. P. 6898 of 1904) obtains neutral sulphate and SO_2 by mixing the nitre-cake with 12 per cent. wood-shavings and 2 per cent. coke, and heating in a retort provided with a stirring arrangement.

Garroway (B. P. 11986 of 1905) decomposes a solution of sodium bisulphite under pressure by sodium bisulphate or free sulphuric acid; most of the SO_2 is driven out in the cold, the remainder by injection of steam.

Elworthy (Fr. P. 352254) oxidises a mixture of sodium sulphide with calcium or sodium sulphate in a Bessemer converter by air, thus obtaining all the S as SO_2.

Basset (Fr. P. 428019) heats a mixture of calcium sulphate and alumina, preferably with addition of powdered coal, to a high temperature. The reaction is: $CaSO_4 + CaS = 4CaO + 4SO_2$.

Schildhaus and Condrea (Amer. P. 956184) obtain SO_2 from acid-tar or sludge by heating it to 200° to 300° in a retort and passing into this air, pre-heated to the same degree; the liquid hydrocarbons contained in the vapours produced are condensed and the remaining gases are washed, first with heavy hydrocarbon oil and finally with sulphuric acid; the coke formed is continuously removed from the retort.

J. S. and A. A. Blowski (Amer. P. 1010221) obtain SO_2 from petroleum sludge by means of water, so as to obtain a dilute acid containing sufficient organic matter to decompose the acid on subsequent heating. The SO_2 thus obtained is purified and reoxidised to attain sulphuric acid.

E. Preparation of Sulphur Dioxide in the Pure or Liquid State.[1]

Formerly pure sulphur dioxide, free from nitrogen and excess of oxygen, was required only in very few cases for industrial purposes. The methods employed for preparing that gas were various, one of the commonest being the action of concentrated sulphuric acid upon copper at a higher temperature. This is, of course, only applicable where there is a sale for the cupric sulphate formed, and is, moreover, hardly workable on a large scale. Cheaper and easier is the process of heating strong sulphuric acid with charcoal, when a mixture of SO_2 with CO_2 (and CO) is obtained:

$$2SO_4H_2 + C = 2H_2O + 2SO_2 + CO_2.$$

The CO and CO_2 are harmless in many applications of SO_2. Sulphur dioxide, quite free from other gases, is made by heating concentrated sulphuric acid with sulphur:

$$2SO_4H_2 + S = 2H_2O + 3SO_2;$$

this can be done by running a slow stream of sulphuric acid on sulphur, heated to about 400° in an iron retort. It should, however, be noticed that melted sulphur acts very strongly upon cast iron; hence another process, privately communicated to me from a trustworthy source, would seem preferable. The operation is performed in a cast-iron pan, widening out at the top so that a lining of acid-resisting bricks can be put in it. Concentrated sulphuric acid is boiled with sulphur, which floats on the top and is kept by the brick lining from coming into immediate contact with the iron, whilst the lower part of the pan is fully exposed to the heating action of the fire.

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[1] A special treatise on the preparation, properties, and application of pure sulphur dioxide is *Flussiges Schwefeldioxyd*, by A. Harpf (Stuttgart, 1900).

Sulphur dioxide was made by the Compagnie industrielle des procédés Raoul Pictet (Ger. P. 22365), and was purified in a special apparatus, utilising the fact that the hydrates of SO_2 all crystallise at −10°, and that gaseous SO_2 at this temperature loses all its aqueous vapour. We refrain from describing this (somewhat complicated) apparatus, which is also described in the *J. Soc. Chem. Ind.*, 1883, p. 413, as the condensation of liquid SO_2 is performed in a much simpler way by the Schroeder and Haenisch process (pp. 533 *et seq.*), which in fact has caused the above-mentioned process to be abandoned.

P. Hart (B. P. 13950 of 1885) prepares pure sulphur dioxide by acting with sulphuric acid of sp. gr. 1·750, on finely ground iron sulphide, both being mixed in a cast-iron retort and heated to over 200° C., when a steady stream of nearly pure SO_2 is evolved.

An old and well-known process for obtaining pure SO_2 is: heating ferrous sulphate with sulphur, in the presence of sufficient air, the reaction being:

$$2FeSO_4 + 2S + 3O = Fe_2O_3 + 4SO_2.$$

This process was made the subject of a new patent by Terrell (B. P. 5930 of 1884), who evidently lays the greatest stress on the ferric oxide remaining behind, which furnishes a good paint.

Ford's process (Amer. P. 363457) consists mainly in burning sulphur by means of air previously dried with sulphuric acid, and passing the gases through a worm, where, by cooling and pressure, liquid SO_2 is condensed. It is difficult to see any novelty whatever in this process.

Bergmann and Berliner (Ger. P. 160940) prepare pure SO_2 by a reaction observed by Gerland, viz:—the absorption by calcium diphosphate, which, on heating to 100°, liberates the SO_2 again. Dicalciumphosphate absorbs SO_2 even from very dilute mixtures, like fuel gases and exit gases of acid works, which may thus be utilised, the absorbent being always recovered. The reactions are:—

1. $2CaHPO_4 + 2SO_2 + 2H_2O = CaH_4(PO_4)_2 + Ca(HSO_3)_2$.
2. $CaH_4(PO_4)_2 + Ca(HSO_3)_2 = 2CaHPO_4 + 2SO_2 + 2H_2O$.

Carpenter (Amer. P. 829765) obtains pure SO_2 from burner gases by gradual cooling, moistening with water, thus separating the mechanical impurities, and cooling down to 0°, whereby the SO_2 condenses as a solution in water, while the other gases go away.

Marin (Fr. P. 374519) dries gases, especially SO_2, in a vertical cylinder, in which metallic trays are placed, on which calcium chloride or other dehydrating agents are spread [!].

Hegeler and Heinz (Amer. P. 931868) mix hot SO_2 gases from a sulphur burner with about the same quantity of cooled gases, to reduce the temperature below 100°, pass the mixture through a tower fed with water, dry and filter the gases.

Moulin and Vandoni (Fr. P. 432431) describe an apparatus consisting of a sulphur-burner, working preferably under pressure, followed by a heat interchanger, a cooling apparatus, and a series of compressors, where the gas is compressed to about 30 kg., after which it is cooled to about 0° and passed to the liquefier. The residual gases from this, after allowing to expand to about 5·5 kg. pressure, are at a temperature of −70°, and are used for cooling the tubes of the liquefier and in the heat interchangers.

The Comp. ind. des Alcools de l'Ardèche (B. P. 9145 of 1909), in order to recover SO_2 from solutions, project these violently in the form of a jet against the walls of a case, after being slightly heated. The SO_2 goes out at the top, the water flows out at the bottom.

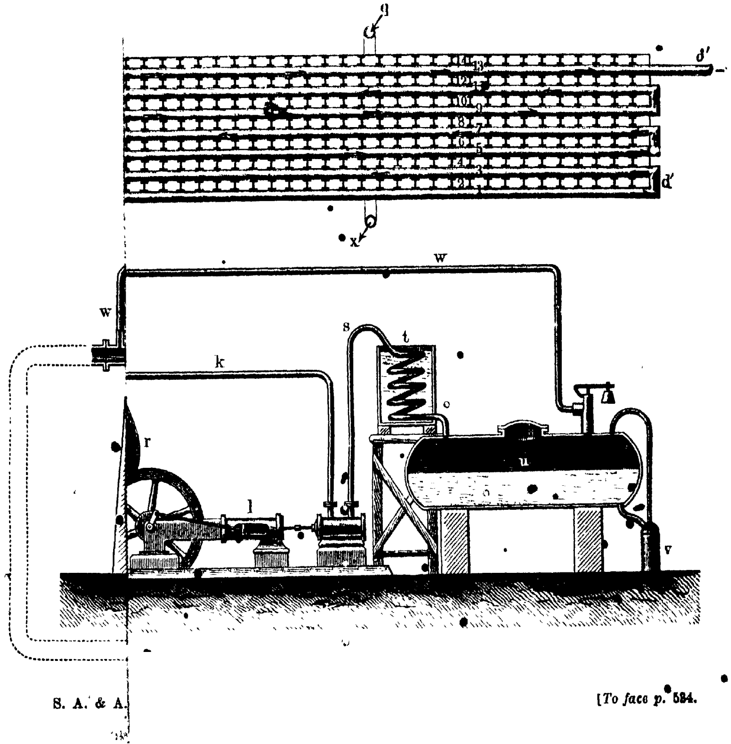
The only process for preparing pure liquid sulphur dioxide at work on the large scale is probably that of Schroeder and Haenisch, which allows of preparing that substance in a cheap way from gases containing down to 4 per cent. SO_2. It is unnecessary to say that richer gases are better for this purpose. This process has made liquid sulphur dioxide a cheap article, manufactured on a large scale, and has rendered it possible to employ that substance for many purposes for which formerly only the ordinary impure gaseous SO_2 was available.

The process of Schroeder and Haenisch, embodied in B. Ps. 2621, 1883; 6404 and 6405, 1885, was first taken up by the firm Wilhelm Grillo (afterwards converted into the Aktiengesellschaft fur Zink-Industrie, vormals Wilhelm Grillo) at their zinc-works at Hamborn, Rhenish Prussia, where, in 1885, an experimental factory was erected, turning out about 12 cwt. liquid sulphur-dioxide per diem. The gases, testing 6 per cent. SO_2, were taken from a novel kind of blende-roasting furnace, similar to the Rhenania furnace described on p. 504 (system Julius Grillo, Ger. P. 28458). In 1886 four such furnaces were combined with a larger plant for 8 tons SO_2 per diem. Very soon after similar factories were erected at Lipine and at Chropaczow, in Upper Silesia, and about 1899 another at Bound Brook, N.J., U.S.A. (The factory at Chropaczow has since been converted into an ordinary sulphuric-acid works.)

The process consists in absorbing water in an ordinary coke-tower, and expelling it again from the resulting weak solution by the action of heat, in such manner that the latent heat of the steam carried along is fully utilised, and ultimately a very small amount of coal is required. It is described by the inventors, apart from the patent-specifications in *Chem. Ind.*, 1884, p. 120; but this description is now antiquated, and we shall here go by later descriptions (*Paper Trade Journal*, 1888; *Z. angew. Chem.*, 1888, p. 488), by my personal observations of the work as practically carried out, and by notes received from the inventors in 1902.

The burner-gases arrive in the flue *a*, *a* (Fig. 149), and after having lost part or most of their heat by passing underneath the lead pans *c*, *c*, they pass into the coke-tower *b*, where they are treated with such a quantity of cold water that all the SO_2 is condensed (the exit gases contain only 0·05 per cent. SO_2 per volume), and only O and N pass out at *c*. The solution of sulphurous acid, containing about 10 kg. SO_2 per 1000 kg. of liquid, is run out by pipe *d*, and first passes through an apparatus,

FIG. 141.



S. A. & A.

[To face p. 584.

shown separately in Fig. 141, where it receives a previous heating, and then successively through the closed lead pans *e*, *e*, where the heating is continued by the action of the hot burner-gases acting in the flue *a*, *a*. The apparatus, Fig. 141, serves for heating up the cold acid solution by the heat of the spent liquor, resulting at a later stage of the process. It is built up by superposing a number of sheets of lead, 7 lb. per superficial foot, of considerable surface, corresponding to the quantity of acid liquor to be treated. These sheets are combined in such a way as to form a corresponding number of shallow lead chambers, about $1\frac{1}{2}$ in. deep, superposed one over another and connected with each other in the following way:—The acid liquor flows through *d* into the bottom chamber from left to right; through a side connection *d′*, occupying the whole length of the lateral edge, it is conveyed into the third chamber, from here through δ'' into chamber 5, and thus further cools the 7th chamber, 9th, and so forth, issuing at δ'. The chambers Nos. 2, 4, 6, 8, and so forth, serve in the same way for running down the hot spent liquor obtained at a later stage of the process. This liquor, which enters at *q*, always flows in a direction at right angles to that of the acid liquor rising up in the alternate chambers, so that the connections for the spent liquor flowing down are situate in the front and back part of apparatus, Fig. 141. In order to prevent a sagging of the plates, strips of lead are arranged in each chamber as stays, running in each chamber in the direction of the current of liquor. The thin sheets of lead being good conductors of heat, the cold acid liquor, on rising through chambers 1, 3, 5, 7, etc., is gradually heated up, whilst the hot spent liquor, descending through the intermediate chambers, gives off its heat. Of course there must always be a certain difference of temperature and loss of heat, depending upon the duration of contact, the depth of the liquid, and the speed of the current. With chambers of $1\frac{1}{2}$ or 2 in. depth, and counter currents lasting ten or twelve minutes, and sufficiently large surfaces, the difference of temperature will be about 10°; that is, the cold acid liquor will be heated up from 15° to 85° C., whilst the hot spent liquor goes down from 95° to 25° C. In practice the heating up rises to 95°, and the cooling liquid descends to 50°. The cold spent liquor is run to waste through *x*.

Later on (1902) the flat lead chambers, where leaks are not easily discovered and repaired, were replaced by a set of small lead cylinders working on the system of gradual heat-exchange (counter-current).

The heated-up acid liquor now travels successively through the covered lead pans *e*, *e*, where the heating is continued as mentioned before, so that the boiling-point is attained. The gases and vapours here evolved are conducted through pipe *f* into the water-cooled worm *g*, and from here through the pipe *h* into the tower *i*, where the last remaining admixture of moisture is taken out by dry calcium chloride or (preferably) by coke moistened with strong sulphuric acid. From here the dry sulphur dioxide passes through pipe *k* into the pump *l*. The liquor heated to boiling in the pans *e*, *e*, which still contains some SO_2, passes through pipe *m* into the column *n*, where the steam is to a great extent condensed by injection of cold water, whilst nearly dry SO_2 passes up in *p*, and thus equally gets into worm *g* and further on into the pump *l*. The column *n* is shown in some detail, as described in a further patent by Schroeder and Haenisch (Ger. P. 36721), which refers to the separation of steam from its mixture with SO_2, and as this is a matter of general importance, we shall give their statements at some length. It is not easy to separate large quantities of aqueous vapour from a mixture with gaseous SO_2. Indirect cooling by outward application of cold water requires a very large leaden apparatus, and the effect is but partial, as the vapours pass without hindrance through the central parts of the worms or other kind of apparatus. Moreover the condensed water, unless the temperature of the cooling-apparatus is kept nearly at a boiling heat, carries down very much SO_2. The new process effects the removal of the steam from the aforesaid gaseous mixture by direct injection of water, which certainly at first condenses a good deal of SO_2. But if the acid solution thus formed is made in a systematic manner to meet the hot mixture of aqueous vapour and SO_2, its temperature will be gradually raised and will ultimately attain boiling heat, and *pari passu* its percentage of SO_2 will decrease, so that at 100° it is nearly at zero. The following table shows the diminution of the percentage of SO_2 with the rise of temperature :—

Percentage of a saturated solution of SO_2:—

At 20° C. = 8·6 per cent. SO_2.
,, 30° C. = 7·4 ,, ,, ,,
,, 40° C. = 6·1 ,, ,, ,,
,, 50° C. = 4·9 ,, ,, ,,
,, 60° C. = 3·7 ,, ,, ,,
,, 70° C. = 2·6 ,, ,, ,,
,, 80° C. = 1·7 ,, ,, ,,
,, 90° C. = 0·9 ,, ,, ,,
,, 100° C. = 0·1 ,, ,, ,,

If the injection of water is so adjusted that the liquid running off is at a temperature of 95° or 100° C., the latter cannot, as shown by the preceding table, carry away any considerable quantity of SO_2. On the other hand, if the course traversed is long enough, the steam must be completely condensed by the cold water injected.

This process is carried out in the apparatus shown in Fig. 142, viz. a leaden column, filled in the lower part with stoneware diaphragms, in the upper part with coke. The mixture of steam and SO_2 enters through pipe *a* and rises in the tower. Cold water is injected by the rose *b*, condensing both water and SO_2, and flowing down as an aqueous solution of sulphurous acid. On reaching the lower parts, it meets continually fresh quantities

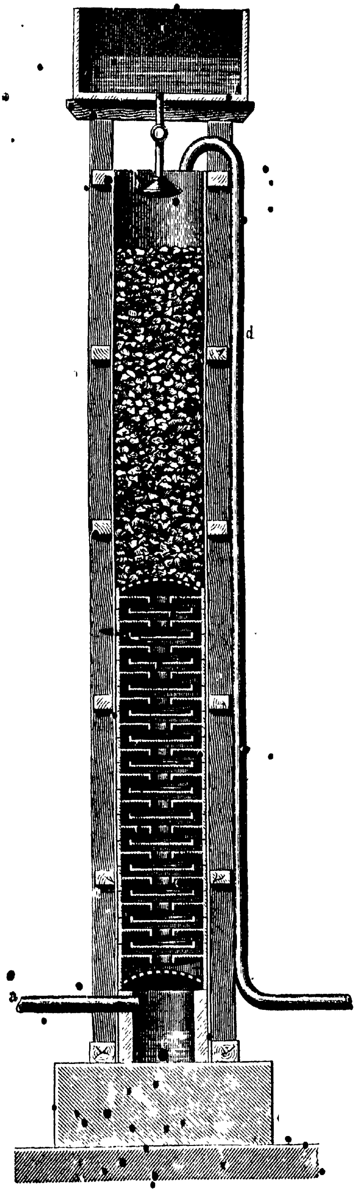


FIG. 142.

of hot gases and vapours, and arrives at the bottom 100° C. hot. It there yields up again the SO_2 absorbed higher up, and at the bottom pipe *c* carries off both the injected water and that condensed from the steam. After some time of working, and with proper regulation of the feed, the temperature of the water from the top downwards rises regularly to a boiling heat, and its percentage of SO_2 diminishes at the same ratio; but the quantity of SO_2 in the upper region is so considerable that the injected water cannot retain it all, and pipe *d* carries away a continuous stream of gaseous SO_2 deprived of steam. The dish shape of the stoneware parts in the lower half of the tower has the advantage of retaining the descending liquor for some time, and exposing it to the heat of the rising steam; but instead of this, coke may be used all over, if the tower is made high enough.

Returning to Fig. 139, we see that the water condensed in the worm *g* finds its way equally into column *n*, and is deprived of its SO_2 there. The hot spent liquor runs off at the bottom by pipe *q*, and is utilised, as explained before, for heating up the cold acid liquor in the apparatus, Fig. 140, where the entrance to the pipe *q* is visible. In order to regulate the compression of the gaseous sulphur dioxide to a liquid, a taffeta bag, *r*, is interposed in pipe *k*, and the motion of pump *l* is regulated according to the size of this bag. The compressed gas enters through *s* into the worm *t*, and is liquefied there by cooling and pressure, the latter depending upon the temperature of the cooling-water, *e.g.* 1·26 atm. at 10°, 2·24 atm. at 20°, 3·51 atm. at 30°, etc. From *t* the liquid runs into the wrought-iron reservoir *u*, from which it is drawn off into the iron bottles, *v*, or into tank-waggons. In order to get rid of the carried-along portions of oxygen and nitrogen, the boiler, *u*, is provided with an outlet-pipe, *w*, connected with *u* by a valve; the gases from here are conducted back into the absorbing-tower *b*.

Haenisch has also described an improved column for boiling the solution of SO_2 (Ger. P. 52025). In 1899 a factory in Silesia produced 1266 tons liquid SO_2 by the above process from zinc-blende gases; the production of the other works is not known. The cost price is supposed to be £2 per ton (on somewhat arbitrary data); the selling price ten years ago was £5 to £5, 10s. at the works.

Carriage of Liquid Sulphur Dioxide.

The liquid sulphur dioxide is sent out in iron cylinders (bottles) holding 1 or 2 cwt. each, or in tank-waggons of 10 tons capacity. The former are shown in Figs. 143 and 144. When sent out, the outlet valve is protected by a cap *a*. Before use this is removed, as well as the small cap fixed on the neck *b*. If now the plug of the screw-valve, *c*, is turned by means of a key, the sulphur dioxide escapes in gaseous form through the opening in *b*. The stuffing-box or the whole valve must *not* be removed. After a time the evaporation of SO_2 lowers the temperature to −10° C., so that no more gas is given off till the apparatus has taken up heat from without.

If the sulphur dioxide is to be got out in the liquid form, the vessel is put on its side (Fig. 144) in such a position that neck *b* is at the top side. The pressure of its vapour now forces the SO_2 out of *b*. The bent tube within the vessel admits of emptying it entirely of liquid SO_2. This substance can be conveyed away by a lead pipe, screwed on to *b*, or even by an india-rubber pipe. The bottles are tested to 50 atm. pressure, so that there is no danger whatever in their transit, as the vapour-tension of SO_2 amounts to:—

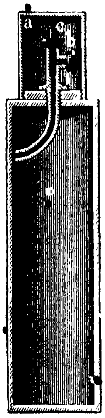


FIG. 143.

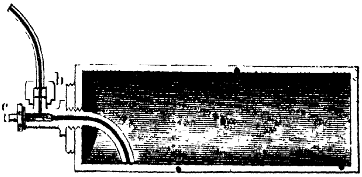


FIG. 144.

0	atmosphere overpressure	at	−10° C.
0·53	,,	,,	,,	0°
1·26	,,	,,	,,	+10°
2·24	atmospheres	,,	,,	20°
3·51	,,	,,	,,	30°
5·15	,,	,,	,,	40°

Still it is advisable not to keep the liquid in a place whose temperature may rise upwards of 40° C.

To prevent over-filling, in view of the expansion by heat, the bottles should not be filled more than nine-tenths, which is ascertained, both by weighing them and by prolonging the outlet-tube inside to one-tenth of the depth of the vessel; when opening the valve only gas, no liquid, should escape. These bottles are usually made to hold 100 kg., exceptionally 500 kg. Besides, tank-waggons are used for 10 tons liquid sulphur dioxide, contained in three wrought-iron welded cylinders, about 23 ft. long and 2 ft. 3 in. diameter, tested for 30 atm.

Boake and Roberts (B. P. 19789 of 1892) find that liquid SO_2 does not act on tin or soft solder, and that therefore these can be employed in the manufacture of carrying-vessels.

Carrier (Fr. P. 402810) describes a pump specially adapted for the compression of sulphur dioxide.

Pacottet (Fr. P. 365224) describes an apparatus for measuring liquid SO_2, which he calls sulphitometer.

Soy (B. P. 12276 of 1893) patents the process of sending out liquid SO_2 in glass vessels sealed by the blowpipe, to be broken by a hammer in the rooms to be disinfected.

The principal *uses for liquid sulphur dioxide* are for refrigerating-machines (Pictet's and others), for wood-pulp manufacture (to bring the calcium bisulphite liquors up to strength), for the purification of beetroot juice, for disinfecting, for bleaching, for the manufacture of glue and gelatine.

Liquid sulphur dioxide has been applied by Behrend and Zimmermann as a means for increasing the efficiency of steam-engines by utilising the heat of the exhaust steam for evaporating SO_2. The high-pressure vapours thus produced are utilised in an auxiliary cylinder for generating motive power, and are afterwards again condensed to liquid SO_2. Hitherto this system does not seem to have fulfilled its expectations.

The formerly rather extensive use of liquid SO_2 for bringing calcium bisulphite liquor (for the manufacture of wood-pulp) up to strength has very much decreased, since the factories have improved their plant for the direct preparation of strong sulphite liquor.

The employment of the strong SO_2 obtained by the Schroeder and Haenisch process for manufacturing sulphuric anhydride (fuming Q.V.) will be mentioned in Chapter XI.

The analysis of liquid sulphur dioxide is described in Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i. p. 305.

F. Draught-pipes and Flues. Removal of Flue-dust and other Impurities.

The flues conveying the burner-gases from the kilns into the chambers or into the Glover towers may be constructed of brickwork only so far as the gases keep hot enough not to allow any moisture whatever to condense, that is especially in upright flues and flue-dust chambers. From this point they must be made of cast iron, and further on, when they have cooled down, of lead.

The gas, which goes away red-hot from the burners, must necessarily be *cooled down* to the temperature of the chambers, say 60° or 80° C.; otherwise the first chamber would be very quickly destroyed. This cooling was formerly effected by conveying the burner-gas in very long flues of cast iron, or partly of cast iron, and, when partially cooled, of lead. Such cooling-flues were made up to 300 ft. long.

The cast-iron pipes are suitably shaped, as shown in Fig. 145, in order that the upper half may be replaced independently of the lower, or taken away for cleaning; the latter can also be done by means of manholes. For a set of from 12 to 18 burners a pipe of 2 ft. diameter is sufficient; but they are now and then made upwards of 3 ft. in diameter. Sometimes they are lined with fire-bricks, as shown in Fig. 146; the cooling in this case is very imperfect and the cost higher. Occasionally, in very large works, square or oblong flues of wrought or cast iron are found. Brick flues (for perpendicular shafts or for

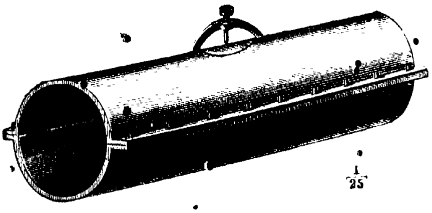


FIG. 145.

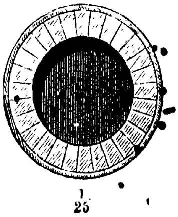


FIG. 146.

flue-dust chambers) are made of bricks boiled in tar, and set with tar and sand. Earthenware pipes mostly crack too quickly.

Perpendicular stacks and pipes act as a sort of chimney, and they are therefore carried up nearly to the top of the chambers where there is no Glover tower. These pipes were sometimes outwardly cooled by water, and even very complicated contrivances were met with for this purpose. It has long been recognised that the only rational way of cooling the burner-gas is this: taking away its heat for some useful purpose, and this is almost everywhere done in the Glover tower (Chapter VI.). Apart from this, the heat of the burner-gas is occasionally utilised for concentrating acid in lead pans (Chapters IV. and IX.).

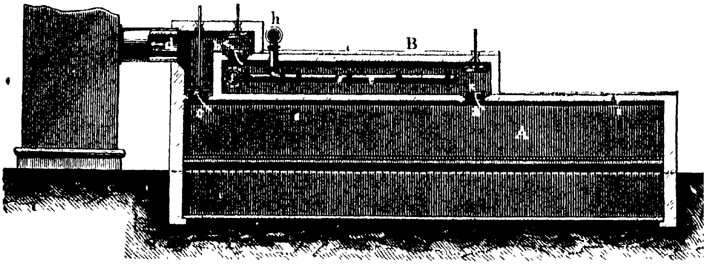


FIG. 147.

Sometimes other ways of disposing of this heat are employed. Thus at the manure-works of Messrs H. and E. Albert, at Biebrich-on-the-Rhine (see Fig. 147), each pyrites-kiln, A, is surmounted by a gas-chamber, B; the burner-gases enter by the holes *a*, provided with shut-off valves, and through similar openings, *b*, get into the pipe *d*, leading to the Glover tower C; a third opening, *c*, permits sending the gas direct into *d* and C. In each of the chambers B there are horizontal cast-iron pipes, *e*, branching off from a main pipe *f*, into which air is forced by a fan-blast. This air, being exposed to the hot burner-gases, becomes hot itself, and leaves the chambers in order to be carried away by the main pipe *h*. This heated air is then conveyed to drying-stoves, where the superphosphate is dried by its action. At Albert's works the temperature of the air is brought to 100° C., but it may be kept cooler or hotter (up to

135°) by regulating the speed of the fan-blast. The burner-gas, entering through *d* into the Glover tower C, is still hot enough to do all the concentrating and denitrating work required; the Glover towers are not so overheated and require less repairs than formerly; the acid flows from them only at 115° to 120°, against 140° as before the new arrangement, and requires less cooling for the Gay-Lussac towers. The saving in coals for the drying-stoves is 5 tons per diem (*cf.* the description, with further diagrams, in *Z. angew. Chem.*, 1889, p. 287; also B. P. of Albert, Fellner, and Ziegler, 15980 of 1888).

Schlippenbach (Ger. P. 225421) conducts pyrites-burner gas of very different composition, obtained in different places at the same time, to two separate collecting-places, so that each of them receives an uninterrupted current of gas of the same composition; thereupon these two gas currents are suitably mixed and passed on to the acid-chambers.

The same object is pursued in the Amer. P. 962498 of Channing and Falding for utilising the gases obtained in the "pyritic smelting" of sulphide copper ores.

The Tentelewsche Chemische Fabrik (Ger. P. 244838) cools pyrites-burner gases by means of a tower, with gas-inlet at the top and outlet at the bottom, surrounded by a cooling-jacket, and filled with perpendicular hollow plates in connection with that jacket. The British patent for this process has been taken out by Eschellmann and Harmuth (B. P. 14670 of 1911).

Purification of Burner-gases from Flue-dust.

In the gas-flues and draught-pipes flue-dust is always deposited, much more when smalls are burnt than with lump ore, especially in furnaces where the small ore is moved about. In such cases special dust-chambers are indispensable, as has been remarked in the description of those furnaces. Even when burning ore in large lumps the flues and pipes must be cleaned out from time to time, as they would otherwise be stopped up entirely. At some factories this is done monthly, at others more rarely. If the deposit is allowed to remain too long, it hardens into a stone-like mass, which cannot be got out without stopping the process.

The composition of this deposit varies, of course, very much; and even its external aspect varies from that of a dry, light dust, to that of a thick, strongly acid mud. It generally contains a large proportion of *arsenic*. Clapham analysed such a deposit, from a source not mentioned (Richardson and Watts, *Chem. Techn.*, i. 3, p. 70), and found:—

Sand, etc.	2·333
Lead oxide	1·683
Ferric oxide	3·700
Cupric oxide	trace
Zinc oxide	trace
Arsenious acid	58·777
Sulphuric acid	25·266
Nitric acid	trace
Water	8·000
	99·759

D. Playfair (*Chem. News*, xxxix. p. 245) examined flue-dust from pyrites-kilns, in which he found chiefly arsenic, antimony, lead, copper, and iron; of thallium 0·002 to 0·05, of tellurium and selenium 0·001 per cent. was present. He describes in detail the analytical methods employed.

Reich (*Erdmann's Journal*, xc. p. 176) found in the Mulden Works a crystallised deposit consisting of equal molecules of arsenious and sulphuric anhydride. Similar deposits have been frequently observed since.

In other cases the deposit is dry dust, mostly consisting of mechanically conveyed pyrites-dust, better burnt than that within the burner itself (Bode, *Beitrage*, p. 41), and nearly always containing so much arsenic that its crystals can be seen with the naked eye.

H. A. Smith (*Chemistry of Sulphuric-Acid-making*) found in the dust 46·36 per cent. of As_2O_3, together with a large quantity of sulphur in the pasty condition—the latter, of course, formed by sublimation from pyrites.

The flue-dust is also a principal source of *thallium*, as we shall see; and when *selenium* occurs in the pyrites it is found in the flue-dust.

Bismuth, to the extent of 3·5 to 4·0 per cent., has been found in the flue-dust from Rio Tinto ore by E. Gibbon (*Chem. Trade J.*, 1905, xxxvi., p. 88), who proposes to recover it by extracting the dust with hydrochloric acid sp. gr. 1·07, allowing the solution to clear, precipitating the bismuth as oxychloride,

$BiOCl$, by dilution with water, heating and agitating, and at last filter-pressing and washing the precipitate.

The flue-dust from the roasting of blende is, of course, quite differently composed from that formed in burning pyrites. Such flue-dust contains (*Fischer's Jahresber.*, 1882, p. 273):—

	I.		II.	
Zinc oxide, insoluble	8·40	26·20	8·20	20·20
,, in soluble combination	17·80		12·00	
Ferrous oxide, soluble	2·16		2·52	
Ferric oxide, ,,	2·40		4·20	
Lead oxide	3·38		4·26	
Sulphuric acid, insoluble	6·46	24·89	8·04	26·88
,, soluble	20·43		18·84	
Water	6·59		9·00	
Residue (chiefly ferric oxide)	31·80		32·42	
	99·42		99·48	

Flue-dust from the St Mardy Tinto Santarossa pyrites (*cf.* Lunge and Banziger, *suprà*, p. 80) contained sulphur: sulphur free 0·13 per cent.; ditto as sulphide 1·48; SO_2 as free sulphuric acid and sulphates 16·31; As_2O_3 69·07; Sb_2O_3 1·68; CuO 0·14 Fe_2O_3 2·03; sand 2·65; water, traces of other substances and loss 6·51.

Bellingrodt (*Chem. Zeit.*, 1886, p. 1039) found in the flue-dus from roasting blende at Oberhausen (Rhenish Prussia) a sufficien quantity of *mercury* to make its recovery profitable.

Krause (Ger. P. 55676) washes the flue-dust from blende furnaces, and tries to recover the zinc from the washings b precipitation with alkaline carbonates.

Dust-Chambers.—Where the quantity of flue-dust is very larg as is generally the case with arsenical ores, and with some the burners for pyrites-smalls, the ordinary dust-chambers, whic form simply enlargements of the gas-flue, are not sufficient, an special contrivances must be adopted. This matter has bee thoroughly worked out in the lead-smelting works and oth metallurgical establishments, and a large number of apparatu have been constructed for this purpose. A very complet synopsis of this is given in the pamphlet by C. A. Hering: *D Verdichtung des Huttenrauchs* (Stuttgart, 1888), pp. 8-36. Ma of the contrivances employed at lead-works, etc., are unsuitab for pyrites, on account of being made of iron. But the gener principles remain the same: the flue-dust must be made to deposit by cooling, by retarding the speed of the gaseous current, and by offering to it large surfaces to which it can attach itself. All these conditions are more or less fulfilled by making the gas-flues adequately long and wide, but this is not sufficient in many cases, especially for arsenical ores. The case is here complicated by the fact that the cooling of the gas may be injurious to the chamber process, and that the long flues, especially those carried in a zigzag way or provided with "baffle-walls," interfere very seriously with the draught. The latter disadvantage has been greatly lessened, since it has been recognised that it is unnecessary to carry the gases in flues like those sketched in Figs. 148 and 149 (in the former the diagram may be taken either as plan or elevation), where the current of gas is constantly checked by meeting solid surfaces, but that the surfaces may be disposed in the direction of the current itself, where they cause the dust to be deposited on them without interfering with the draught. Fig. 150 shows

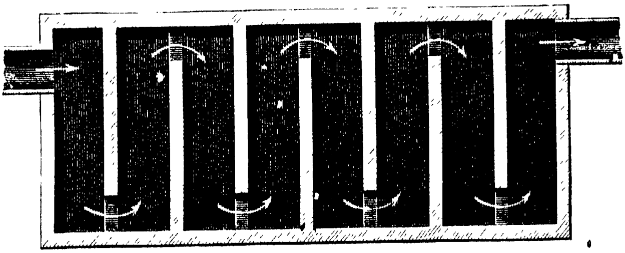


FIG. 148.

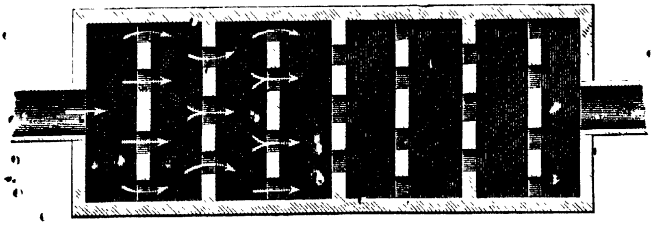


FIG. 149.

how this can be done in such a way that the flue-dust can be removed without interfering with the process. The gases arriving through *a* are, by means of dampers, sent either through chamber A or B. In the present case, the dampers, *b*, *b*, being closed, the gases travel through A. Each chamber is divided into several longitudinal channels by thin partitions, *d*, *d*, made of masonry, fireclay slabs, lead, or other suitable material. The gas thus travels in parallel streams, without any check than that of the indispensable friction, and the streams collect again into one, issuing at *e*. When chamber A is too much choked up by dust, the dampers *b*, *b* are opened, the dampers *c*, *c* are shut, and the gases now travel through B,

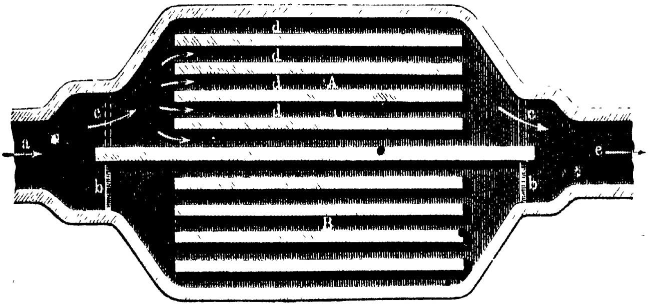


FIG. 150.

giving an opportunity to clean out chamber A by means of suitable manholes.

In very bad cases, as, for instance, with mechanical dust-burners, longitudinal partitions are not sufficient, and real baffle-plates must be employed, as shown in Figs. 148 and 149, and very much multiplied in Figs. 114 and 115 (p. 481). In such cases the loss of draught must be sometimes compensated by mechanical means.

In many cases, where very large quantities of flue-dust have to be dealt with, the gases must be *cooled* artificially. This wa done at the Freiberg works by a special kind of lead flue, coole by water, as sketched in Figs. 151 and 152, the first of whic represents a longitudinal section on the line A B, the second sectional plan on the line C D. The sides of the flue ar formed by a number of oblong pipes, *a*, *a*, joined together a their narrow ends. On the top there is a shallow trough, *b*, supplied with a constant stream of water which trickles down through holes, shown in the diagram, into the space *a*, *a*, and from these through other holes into the common channel *c*, running lengthways. The bottom of the flue is not water-cooled, but as it rests on the small pillars *d*, *d* it is exposed to the action of the air. These flues are very expensive to build, but they have been found to do their work very well indeed,

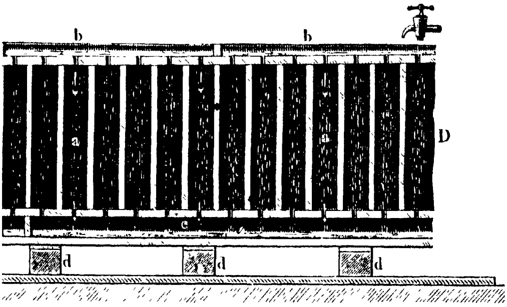


FIG. 151.

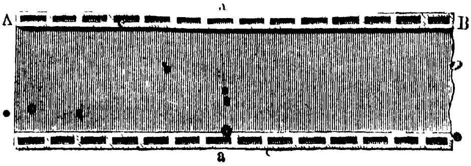


FIG. 152.

and they need next to no repairs (detailed in the *Freiberger Jahrbuch*, 1879, p. 151, table xii.). Of the 2 or 3½ per cent. of arsenic contained in the Freiberg ores, by far the greatest portion (97 per cent.) is condensed in these long flues, where the gases are ultimately cooled down to the temperature of the outer air.

Bauer (*Jahresber. f. Berg- u. Huttenw.*, 1894, p. 39) states that the nine sets of chambers connected with the Freiberg smelting-works (containing thirty lead chambers) possess 8037 m. of flues, of 3·8 sq. m. section. The flue-dust in 1893 contained 1137 kg. silver, 1656 tons lead and 917 tons arsenic, valued at £13,600. Eighty per cent. of the dust was recovered, 20 per cent. has hitherto been lost. The damages to be paid had diminished from £3050 to £180. In that year new flues on the Monier-Freudenberg system were built for recovering the last 20 per cent. of dust. The rate of cooling of the gases was 1° C. per 8·3 m. length in closed-in Monier flues, per 4·5 m. in freely exposed Monier flues, per 3 m. in leaden flues, and per 6 m. in brick flues.

In 1902 I was informed that the water-covered flues have been abandoned at Freiberg as being too costly, and have been replaced by simple lead tunnels. Where the heat is too great for the stability of the latter, brick flues are employed.

Falding (*Min. Ind.*, ix. p. 623) describes a dust-catcher, constructed by A. P. O'Brien, of Richmond, Va., on the well-known centrifugal principle. It works in connection with the cast-iron fan of the same inventor, described in Chapter VI., and receives the gas from five Herreshoff fines furnaces, retaining 75 per cent. of the dust. At the same time it does very efficient service as a nitre-oven. As shown in Figs. 153 and 154, it consists of a tapering, hopper-shaped iron shell, 8 ft. wide in the cylindrical part and 12 ft. high, with a 6-in. opening in the bottom for the discharge of flue-dust. It is lined with 4 in. firebrick. The gas enters through the top pipe at a high rate of speed from the fan and strikes the cylinder tangentially; it leaves the apparatus through a central pipe. The gas takes a rotary motion and deposits all the heavy dust, which is automatically discharged through the 6-in. opening. Six tubular nitre-pots are arranged in the manner shown, so that they can be charged from the top and discharged sideways.

Morton and the United Alkali Co. (B. P. 17461 of 1906) remove flue-dust, *e.g.* from Herreshoff furnaces, which consists chiefly of magnetic oxide of iron, by means of a number of plates of magnetic metal, placed side by side in the flue, on either side of which there is a pole of an electro-magnet. From time to time the electric current is interrupted, whereupon the dust collected on the plates falls into a hopper below.

The Metallic Compounds Separation Syndicate (Ger. P. 153641) combine a number of burners with a common chamber, in which the dust is precipitated by serpentine channels.

Shields (B. Ps. 16353 and 16354 of 1904; Ger. Ps. 180070 and 180071) conducts the burner-gases beneath or into a constantly replenished heap of porous or granular material, such as coke, crushed slag, or the like, which, as it collects the dust, is drawn away from the bottom of the heap by a conveyer, and is elevated to pass into a separator for the removal of the dust, and then restored through a funnel hopper in a clean, hot state to the top of the heap. The receptacle for the filtering material is of conical shape, with its apex downwards, and about the centre of the heap the gases are passed in through a pipe immediately under a horizontal disk, beneath which a cavity is thus maintained. Another form of apparatus is also shown, in which the filtering material descends slowly between sets of inclined shelves arranged in a cylindrical or rectangular form.

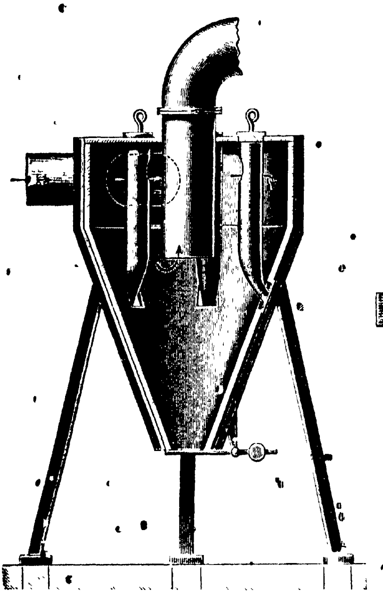


FIG. 153.

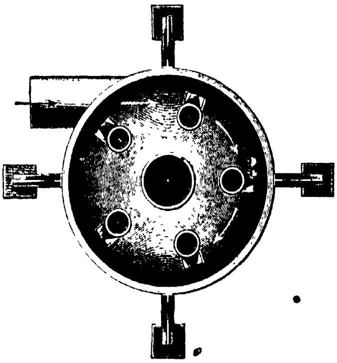


FIG. 154.

Cellarius (B. P. 22080 of 1905) purifies the burner-gases from dust and from nitrous oxides by producing in them, both before entering and after leaving the chambers, a whirling motion and throwing them against a damp clay wall, or against damp coke.

A very complete plant for purifying burner-gases (from mechanical furnaces) from dust is that built by Gilchrist and described by Hartmann and Benker in *Z. angew. Chem.*, 1906, pp. 1188 *et seq.*

The Maschinenfabriken Augsburg and Nurnberg (Ger. P. 169818) blow the gases repeatedly through the purifying apparatus by means of a circular conduct, provided with small outlet openings.

Scheibe (Ger. P. 184038) describes a special form of fans, intended for separating solid or fluid from gaseous particles.

Reese (Amer. P. 989801) cools the gases, scrubs them with sulphuric acid, and passes them through a dry lime filter.

Benker and Hartmann (Fr. P. 387456) pass the burner-gases horizontally through vertical filters composed of pieces of firebricks or stones, contained between vertical perforated walls. The bottom of the filtering column rests on a vertical rotating roller, which continually carries away a small quantity of the filtering-material to a rotating drum, in which it is deprived of the dust with which it is laden. It then falls into a receptacle, from which a conveyer returns it to the top of the filtering-column.

Scherfenberg and Prager (Ger. P 203948) employ dust-chambers with baffling walls, all inner surfaces being corrugated.

Herreshoff (Amer. Ps. 940595 and 940596) passes burner-gases through scrubbing-towers, sprayed with weak acid containing SO_2 and then through filters.

The same inventor (Amer. Ps. 955067 and 969868) washes burner-gases by forming a continuous annular film of sulphuric acid; they may also be cooled during their passage through this.

Brandenburg (*Z. angew. Chem.*, 1909, pp. 2490-2492) describes a centrifugal dust-catcher similar to those which have been found very efficient in connection with blast-furnaces.

Wright (*Eng. and Min. J.*, 1910, p. 111) found in the gases from mechanical dust-burners, after they had traversed a small dust-chamber with a velocity of 1 ft. per second, still 0·28 g. dust per cubic metre; and, after passing through a washing-tower and a long tube, still 0·11 gram.

Gayer and Witter (Ger. P. 227387) employ a box with a horizontal shaft, provided with beating-arms, revolving several hundred times per minute, and moistened by water-sprays. The beaters are placed on the shaft in a screw-line. The gases enter at the bottom and go out at the top.

Heine (Ger. P. 230182) arranges in the dust-chamber slanting plates, reaching a little more than half-way through, and leaving a distance of 3 or 4 mm. from the side free for a small portion of the gases to pass through, so that whirls are formed.

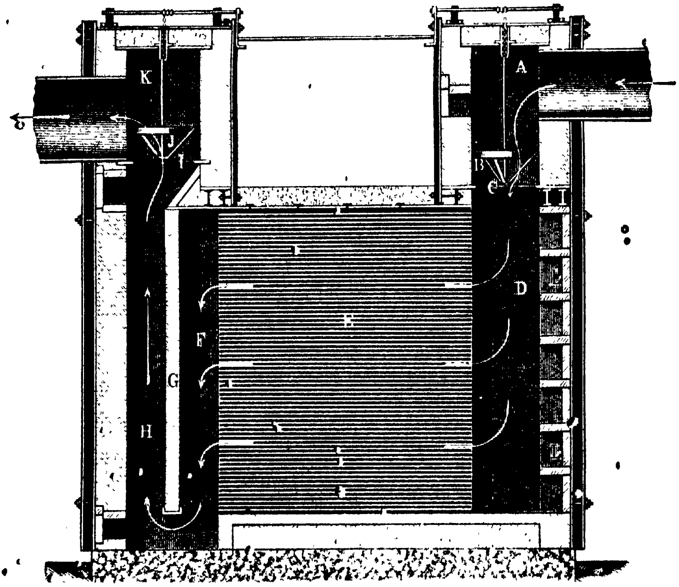


Fig. 155.

Krowatschek (Ger. P. appl. K45381 of 1911) describes a very similar arrangement.

Howard (Amer. P. 896111; re-issue 8th March and 13th September 1910; this patent is held by the General Chemical Co. of New York) describes a dust-separator containing a great number of horizontal steel plates between which the gases pass from one side to the other. It is shown in Fig. 155, and consists of: A, brick entrance flue; B, cast-iron damper, operated from without; C, cast-iron ring-plate over which B closes; D, vestibule from which the gas enters between the horizontal steel plates, E, 2½ in. apart from one another, and gets into space F. They strike against the baffle-wall G, and leave through the flue H, covered by the cast-iron plate I, provided with an opening for the damper J; K is the outlet; L, cleaning-holes with covers. The outside brick walls are 19 in. thick, with a 1 in. insulating space. The interior walls are 12 in. red brick.

The velocity of the gas in passing between the steel plates is checked by the large area of cross-section, and, since these plates are only 2½ in. apart, each dust particle needs to fall only 2½ in. (instead of 6 or 8 ft. as in the old-fashioned practice) before finding a surface on which it sticks. Under ordinary circumstances the plates need not be cleaned any oftener than once in thirty or forty days. For that purpose the covers are removed from the clearing-holes L, and the dust is taken out.

These separators are made for a capacity of 24,000 to 60,000 lb. of ore per day in two compartments, or from 72,000 to 80,000 lb. in four compartments. There are five sizes, with from 6540 to 18,700 superficial ft. of plate area, and a vertical height of from 27 to 31 ft.; ground space required 17 to 31 × 27 ft.

The Purification of Burner-gases from Liquid and Gaseous Contaminations.

This is a very necessary matter where the gases are to serve for the manufacture of SO_3 by contact processes, and we shall in the chapter dealing with these processes make frequent mention of processes for the purification of such gases.

In this chapter we only treat of the purification of burner-gases for ordinary purposes (lead chambers, manufacture of liquid sulphur dioxide, of sulphites, etc.). The *mechanical* impurities are frequently mentioned in other places, especially in connection with the Glover tower, and are dealt with, in the first instance, by dust-chambers (p. 545). But for some purposes this is not sufficient, and, moreover, a *chemical* purification is necessary for various uses of the burner-gases. The Metallurgische Gesellschaft, Frankfort (Ger. P. 161017), describe a process for the uninterrupted simultaneous mechanical and chemical purification and cooling of burner-gases. They employ a water-fed tower, provided with inside shelves, with a vessel placed about midways, where there is not yet much sulphuric acid dissolved in the water run in at the top. Up to that point the water has principally performed a cooling action and a mechanical purification upon the gases; it runs out from the above-mentioned vessel through an overflow, and part of it, after cooling, is used over again in the upper part of the tower, another portion being sprayed into the lower part, for the purpose of chemical purification of the gas. The quantity of water used here is regulated in such manner that it comes to about 70°, at which temperature it absorbs hardly any SO_2 and carries away merely sulphuric acid and ferric-oxide mud.

The Tentelewsche Chemische Fabrik (Ger. P. 194176) purifies the burner-gases from *chlorine*, etc., by first applying a dust-chamber and a water cooler, then taking out the sulphuric-acid fog and the last portions of dust by a coke filter, and ultimately removing the chlorine by a solution of alkali or milk of lime. A special description of their filter is found in Ger. P. 230585.

The same firm (Fr. P. 431067) purifies gases from pyrites-burners as follows. A circular tower, built in sections, is surrounded by an annular space for cooling-water, which connects with hollow vertical partitions crossing each section, the whole being built of lead and supported over a circular trough in which it is sealed by sulphuric acid. The gases from the burners enter from the top and leave at the bottom, whilst the cooling-water passes in the opposite direction through the cylindrical jacket and the hollow partitions. The burner-gases can be cooled from 500° to the ordinary temperature, and all the sulphuric-acid fog they contain separated as a liquid. The lid of the apparatus is removable, and easy access is thus afforded for cleaning, which, however, is only necessary at long intervals.

Sulphur dioxide gases for the manufacture of wood-pulp ought to be as free as possible, not merely from flue-dust but also from *sulphuric acid* (or *sulphur trioxide*). For this purpose very efficient dust-chambers must be provided; the gas must also be specially cooled, *e.g.* by perpendicular cast-iron pipes, 2 ft. 6 in. diameter, running up for a height of 50 or 60 ft. and down again; they end in a lead-lined pipe provided with a manhole and filled with iron borings. Here the sulphuric acid, which is condensed by the cooling, collects, and is taken up by the iron borings. Provision must be made for removing the solution of ferrous sulphate formed, and for renewing the iron borings as they waste away. (A description of such an apparatus is found in *Papier-Zeit.*, 1894, pp. 2099 and 2130.) A more efficient removal of the SO_3 and H_2SO_4 is effected by the apparatus of Némethy (Ger. P. 48285 of 1889), in which the gases from the burner pass through a large box containing iron borings, etc., before entering the cooling-apparatus (*cf.* p. 407).

Collett and Eckardt (Ger. P. 244841) purify the burner gases, for that purpose, after properly regulating their oxygen contents, by allowing them to act upon ammonium sulphite at a higher temperature, whereby all the ammonium sulphite can be transformed into practically pure sulphate.

Projahn (Ger. P. 221847) purifies burner-gases from *arsenic* by passing them at a high temperature over a porous mass of aluminium sulphate, as it is obtained by heating such sulphate containing water. This mass is placed behind the pyrites or blende roasters, and retains not merely arsenic, but also *selenium* and flue-dust, practically at no expense.

Herreshoff and the General Chemical Co. (Amer. P. 969868) cool and purify pyrites-burner gases by producing between the wall and the gases a pellicle of liquid which also protects the metallic walls against destruction.

Duron (B. P. 9869 of 1910) first takes out the coarsest impurities, especially Fe and As, by filtration through a suitable substance containing ferric sulphate, cooling down in the meantime, then heating and cooling with sprayed sulphuric acid of about 30° Bé, then passing upwards through a scrubbing tower sprinkled with water, then through filter chambers charged with inert materials, and then raising them to the temperature required for the lead-chamber or the contact process by means of a heater arranged within the ordinary purifier and heated by the hot gases to be purified.

Fluorine may get into gases through the presence of fluor-spar in the pyrites, and may do damage to the towers and chambers. Klencke (Fr. P. 408417) removes it by treating the gases with denitrated sulphuric acid in an empty tower, and afterwards by nitrous vitriol in another tower fitted with perforated lead shelves.

Selenium was formerly considered as a non-essential impurity of sulphuric acid, on account of its small quantity. Klason and Mellqvist (*Papier-Zeit.*, 1912, p. 767), however, state that selenium not merely causes the red coloration of Glover- and chamber-acid, but acts in a much more serious way in the manufacture of sulphite cellulose, as has been manifested in the application of Falun pyrites. As little as 1 mg. selenium per litre of acid may, by catalytic action, completely convert the SO_2 into H_2SO_4 and S. Tellurium acts in a similar way, but comes hardly into question, owing to the high boiling-point of the free metal and its oxides. This injurious action of the Falun pyrites has caused some of the Swedish sulphite-cellulose makers to abandon it in favour of Sicilian brimstone.

G. A COMPOSITION OF THE BURNER-GAS.

1. *Composition of the Burner-gas from Burning Brimstone.*

Atmospheric air contains, roughly speaking, 21 per cent. by volume of oxygen, and 79 per cent. nitrogen.[1] If it were possible to convert all the oxygen into sulphur dioxide, the volume would not be changed, since 1 mol. O_2 furnishes 1 mol. SO_2.

In the case of making sulphur dioxide for the manufacture of wood-pulp, we want to render it as free as possible from uncombined oxygen. But for the manufacture of sulphuric acid we must introduce into the burner sufficient oxygen for the subsequent formation of sulphuric acid, and a certain excess is practically necessary in the process. For the former object we must at once increase the oxygen by 50 per cent., as $2SO_2$ require O_2 for the formation of SO_3, and the theoretical maximum of SO_2 in the burner-gas would therefore be 14 per cent., together with 7 per cent. oxygen and 79 per cent. nitrogen. Practically we must have an excess of oxygen equal to 5 per cent. of the exit-gases from the system, together with 95 per cent. N.

If we call the unknown volume in the burner-gas of this excess oxygen $= x$, it must carry along $\frac{79}{21}x$ vols. N. To this are added 79 vols. N, entering together with the 21 vols. O required for forming 14 vols. of SO_2 and converting them into SO_3. The volume of the total N and of the excess oxygen required in practice for each 14 vols. of SO_2 introduced into the chambers thus amounts to

---

[1] Of course this item "nitrogen" comprises argon, helium, and all other indifferent gases recently discovered in atmospheric air. To simplify matters, we shall throughout this book omit the special mention of these gases, which, as far as we know, in sulphuric-acid making play exactly the same inert part as elementary atmospheric nitrogen.

$$79+\frac{79}{21}x+x = 79+\frac{100}{21}x.$$

x was stated to form 5 per cent. $= \frac{1}{20}$ of this volume.

We have thus the equation :—

$$x = \frac{1}{20}\left(79+\frac{100}{21}x\right) = \frac{79}{20}+\frac{5}{21}x.$$

From this follows :—

$$x-\frac{5}{21}x \text{ or } \frac{16}{21}x = \frac{79}{20},$$

$$x = \frac{79\times 21}{20\times 16} = 5{\cdot}18 \text{ vols.};$$

that is, besides the theoretical quantities of gas mentioned above, another 5·18 vols. of oxygen, along with the corresponding $5{\cdot}18\times\frac{79}{21} = 19{\cdot}50$ vols. of nitrogen, are necessary. The gaseous mixture formed in the sulphur-burner accordingly ought to contain upon each

14 vols of SO_2,
7 + 5·18 = 12·18 ,, O, and
79 + 19·50 = 98·50 ,, N.
124·68 vols.

From this the following composition for 1 l. of this gaseous mixture is computed :—

0·1123 litre SO_2
0·0977 ,, O
0·7900 ,, N
1·0000 ,,

That is to say : *The normal quantity of SO_2 in burner-gas from brimstone-burners is 11·23 per cent. by volume.*

This normal quantity can be attained by proper care, but is frequently not reached.

2. *Composition of the Burner-gas from burning Pyrites.*

The proportion of air required in this case differs very much from the preceding. We shall calculate this for pure iron disulphide. This body consists of 46·66 per cent. Fe and 53·33 per cent. S.

Although in the combustion of dense pyrites sometimes the iron is not all oxidised up to Fe_2O_3, and a little magnetic oxide, Fe_3O_4, is formed, we must suppose the complete conversion of iron into Fe_2O_3 as the normal state to be aimed at for complete utilisation of the sulphur. Consequently 2 mols. or 240 parts of FeS_2 require 3 atoms = 48 parts O for oxidising the iron, and another 8 atoms = 128 parts O for burning the S into SO_2. Altogether 11 atoms = 176 parts oxygen are necessary for burning, and another 4 atoms of oxygen = 64 parts for changing the formed 4 mols. = 256 parts of SO_2 into SO_3. From this we calculate that for each thousand parts of FeS_2,

200 parts oxygen are required for oxidising the iron,
533⅓ „ „ „ forming SO_2,
266⅔ „ „ „ oxidising this to SO_3
1000 „ in all.

Now here also an excess of oxygen must be used, even larger than in the case of brimstone, which we will assume to amount to 6·4 per cent. by volume in the gas leaving the chambers. If we call the unknown volume of oxygen in excess to be introduced for each kilogram of S employed as FeS_2, x litre, the volume of nitrogen accompanying it is $\frac{79}{21}x$ litre. Both together and the 4933·3 l. N, introduced along with the O requisite for combustion and formation of SO_3, form the gaseous mixture escaping at the end, the volume of which is therefore

$$4933{\cdot}3 \times x + \frac{79}{21}x = 4933{\cdot}3 + \frac{100}{21}x.$$

As x is $\frac{6{\cdot}4}{100}$ of this volume, we have

$$x = \frac{6.4}{100}\left(4933{\cdot}3 + \frac{100}{21}\right),$$

$$x = 454{\cdot}6.$$

Accordingly for each kilogram of S burnt as FeS_2, apart from the theoretical 6244·7 l. air, another 454·1 l. oxygen, together with $\frac{454.1 \times 79}{21} = 1708.4$ l. nitrogen—that is, 2162·5 l. air—altogether 8407·2 l. air at 0° and 760 mm. pressure, have to be introduced.

Now each kilogram of free sulphur (brimstone) requires 6199 l. air at 0° and 760 mm.; consequently a certain quantity of sulphur, burnt as FeS_2, requires

$$\frac{8407.2}{6199} = 1.356 \text{ times}$$

as much air as if burnt in the free state.

This is not quite the proportion of the gas *as it enters the chambers.* For on burning FeS_2 a portion of the oxygen remains behind with the iron, whilst on burning brimstone the whole quantity of air gets into the chambers, and at equal temperature and pressure retains its volume, since oxygen on combining with S to SO_2 does not change its volume.

The 8407·2 l. air entering the burner for each kilogram of sulphur burnt as FeS_2 produce the following quantities of gas, calculated for 0° and 760 mm.:—

699·4 l. SO_2 generated from the same volume of O,
349·7 „ O required for transforming SO_2 into SO_3,
454·1 „ O as excess,
4933·3 „ N accompanying the theoretically necessary oxygen,
1708·4 „ N „ „ excess of oxygen.
8144·9 l. containing 699·4 l. SO_2,
830·9 „ O,
6641·7 „ N.

For a certain quantity of sulphur, burnt as FeS_2, $\frac{8144.9}{6199}$ times = 1·314 times as much gas must enter the chambers as if the sulphur were burnt in the free state.

Consequently, in the case of burning pyrites, 100 *vols. of the normal gaseous mixture on entering the chamber ought to consist of*

8·59 vols. SO_2,
9·87 „ O,
81·54 „ N.

In most factories the sulphur dioxide is much below 8·59 per cent., sometimes not above 6 per cent. of the volume of the gas. In that case correspondingly less acid is made in the same chamber-space, unless the formation of sulphuric acid is increased by a larger consumption of nitre. We shall return to this subject in Chapter VII.

Sulphur Dioxide for manufacturing Calcium Bisulphite (in the Manufacture of Wood-pulp, etc.).—In this case the conditions are different from those just described. There is no question of having to provide the oxygen for forming H_2SO_4 from SO_2 and the excess of oxygen practically necessary in the lead chambers; and the formation of SO_3 in the burners should be avoided as much as possible. The operation should be conducted so as to exceed as little as possible the amount of oxygen demanded by the equation: $2FeS_2 + 11O = Fe_2O_3 + 4SO_2$, which corresponds to a theoretical maximum of 16 per cent. SO_2 by volume in the burner-gas. Practically, however, 11 per cent. should not be exceeded, because otherwise the burners get too hot, which causes the sublimation of sulphur and the formation of scoria in the burners.

Harpf (Wochenbl. fur Papierfabr., Biberach, 1901, Nos. 23, 25, and 27) gives some calculations referring to this special case, containing nothing of importance.

3. *Comparison of Brimstone and Pyrites as Material for the Manufacture of Sulphuric, etc.*

We have seen above that the burner-gas from brimstone is richer than that from pyrites in the proportion of 1 : 1·314; that is to say, under equal conditions, the gas generated in burning pyrites occupies 1·314 times as much space as if the same quantity of sulphur had been employed as brimstone. From this it directly follows that the gas will also require much more chamber-space; thus, for an equal production of sulphuric acid, the chambers must be about one-third larger if working with pyrites than if working with brimstone. Usually it is assumed that the consumption of nitre has to be increased in a similar ratio; this, however, is not the case, as a properly constructed Gay-Lussac tower retains almost the whole of the nitre-gas, and the excess volume of air is not of great importance. At the present day, indeed, in well-managed works, less nitre is used with pyrites than has ever been used with brimstone.

Leaving the nitre out of consideration, the advantages of using brimstone are:—A somewhat higher yield of acid (see Chapter X.); rather smaller cost of plant, and less trouble with the burners if anything goes wrong; and, above all, much greater purity of the sulphuric acid, especially from iron and arsenic (this is important only for sale acid, not for use in manure-works, alkali-works, etc.).[1] If brimstone could be had at the same price as the sulphur in pyrites, nobody would hesitate for a moment to employ the former; and even a moderately higher price would not deter from this; but where the pyrites-sulphur, as is the case in most industrial countries, only costs half the price of brimstone, or even less, the latter cannot be employed, except for *pure* acid; and even this, when the difference in price is very large, can be more cheaply made from pyrites than from brimstone.

Owing to this cause, the manufacture of brimstone acid in Europe is confined to small factories which make specially pure acid for bleach-works, for manufacturing articles of food, etc. A somewhat considerable number of such factories still exist in England, whilst very few are found in other European countries. But it should be noticed that sometimes acid is sold in England as "brimstone acid," which is in reality made from pyrites and purified from arsenic, or else acid made from spent oxide of gas-works, which is also practically free from arsenic. In the 41*st Report on Alkali Work*, p. 115, one of the inspectors states that in his district only two sets of brimstone burners were working in 1903, against twenty-one sets in use in 1884. In Scotland in 1903, 2878 tons of brimstone were burned, against 104,481 tons pyrites.

In America formerly all sulphuric acid was made from Sicilian brimstone; but the notes given above (pp. 81 *et seq.*) as to the consumption of pyrites in America show that this is rapidly gaining ground.

It is frequently asserted that sulphuric-acid chambers worked with brimstone last very much longer (up to three times) than with pyrites. It is not impossible that there is *some* difference in this respect; but even this is not certain, and at all events the difference in the life of the chambers is nothing like so great as was formerly supposed, and forms no item in the comparison of costs (*cf.* Chapter V.).

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[1] Steele (*J. Soc. Chem. Ind.*, 1910, p. [illegible]) found in a brimstone burner a deposit of crystallised arsenic sulphate, which, however, will be quite an exceptional case.

Sjöstedt (*Eng. and Min. J.*, 1906) maintains that pyrites-burner gas can be got up to 14 per cent. SO_2 with only 2 per cent. free oxygen, and is much better for the manufacture of *sulphite liquors for wood-pulp* than the gas from brimstone burners [?].

4. *Composition of the Gas from Blende-furnaces.*

For burner-gas from *zinc-blende* the following calculation has been made by Hasenclever (*Chem. Ind.*, 1884, p. 79):—Zinc-blende (in the pure state), ZnS, consists of 63 parts Zn + 32 parts S. For burning it into $ZnO + SO_2$, $3 \times 16 = 48$ parts O are required, for converting the SO_2 into SO_3 another 16 O; therefore for 95 ZnS, containing 32 S, altogether 64 O. This means that each kilogram S in zinc-blende requires 2 kg. O, or 1398·7 l. at 0° and 760 mm., together with 5258·0 l. nitrogen = 6656 l. air. In order to make allowance for the 6·4 vols. per cent. of oxygen required to be in excess in the exit-gas we find this by the formula:—

$$n = \frac{6.4}{100}\left(5258 + \frac{100}{21}n\right),$$

=	484·0	l.	oxygen, corresponding to
	1820·7	,,	nitrogen
	2304·7	,,	air

Consequently the normal gaseous mixture in roasting 1 kg. blende consists of:—

699·4	l.	SO_2,
349·7	,,	O for forming SO_3,
484·0	,,	O in excess,
5288·0	,,	N entering with the theoretically necessary oxygen,
1820·7	,,	N ,, ,, excess oxygen,
8641·8	l. of gases.	

This means that 100 vols. of the gas should contain:

8·12	vols.	SO_2,
9·69	,,	O,
82·19	,,	N.

According to information received in 1902 the blende-gases contain only exceptionally less than 6 per cent. SO_2; ordinarily 6 to 7·5 per cent. SO_2 apart from SO_3 (see below).

So far, as we see from Hasenclever's calculation, theory would show that the strongest obtainable burner-gas from blende is not much inferior to that obtainable from pyrites (p. 559). But apart from the fact that here, as well as in the case of pyrites and to some extent even of brimstone, the theoretical figures are undoubtedly interfered with by the formation of sulphuric anhydride, there is, at least in the case of all the older blende furnaces, a far more potent reason why the practical percentage of SO_2 in blende-gases should be far below the theoretical one. Seeing that in those older furnaces only half or at most two-thirds of the sulphur was liberated as SO_2 [and SO_3], that the other half or third remained behind in the state of $ZnSO_4$, and that the nitrogen corresponding to the four atoms of oxygen contained in $ZnSO_4$ diluted the burner-gas, it is easily understood why formerly it was considered *good* work if blende-gases contained 5 or at most 6 per cent. of SO_2. The modern furnaces (pp. 504 *et seq.*) undoubtedly yield better gases, not much inferior to the burner-gas from pyrites.

5. *Sulphuric Anhydride in Burner-gas.*

In the pyrites-burner, besides sulphur dioxide, there is always some sulphuric anhydride formed during the burning. This fact has long been known, and was explained in 1852 by Woehler and Mahla, and again in 1856 by Plattner (*Die metallurgischen Röstprocesse*) after many experiments, in this way—that many substances, one of which (ferric oxide) is present in large quantity in the pyrites-burner, dispose sulphur dioxide to combine with the oxygen of the air to form sulphuric anhydride; as we now express it by "catalytic action." We have already seen, and in Chapter XI. the subject is fully detailed, that this reaction can be used for the production of sulphuric anhydride itself. Another plausible explanation is, that in the cooler parts of the pyrites-burners sulphates of iron are formed, which in the hotter parts again split up into Fe_2O_3 and SO_3. This explanation, however, is not sufficient for Fortman's experiments *Dingl. polyt. J.*, clxxxvii. p. 155), according to which the whole of the fumes of anhydride appear the moment the pyrites take fire. Scheurer-Kestner (*Bull. Soc. Chim.*, 1875, xxiii. p. 437) explained the matter from the well-known fact that ferric oxide can act as an oxidising agent by successively giving up and absorbing oxygen. It is, however, established that even on burning pure sulphur a little sulphur trioxide is formed, as we shall see.

In Fortmann's experiments, made on a small scale, on burning pyrites far more SO_3 than SO_2 was formed, viz. in one experiment 4 times as much, in another as 5 : 3. His results were evidently altogether wrong, in consequence of a faulty analytical method. Scheurer-Kestner (*loc. cit.*) only found 2 or 3 per cent. of all the SO_2 converted into SO_3, but a larger deficiency of oxygen in the gas than corresponds to this amount; and the subsequent discussion between Bode (*Dingl. polyt. J.*, ccxviii. p. 325) and Scheurer-Kestner (*ibid.*, ccxix. p. 512) did not clear up the matter.

In order to decide the question of the formation of SO_3 on burning pyrites by more exact methods than those hitherto used, especially by Fortmann, I made, together with Salathé, a series of experiments (*Ber.*, x. p. 1824). It was found that SO_2 cannot, as Scheurer-Kestner had supposed, be absorbed and estimated by barium chloride, because even chemically pure SO_2 with $BaCl_2$ in the presence of O or atmospheric air at once gives a precipitate of $BaSO_4$. Check tests proved that exact results were obtained by conducting the gas through an excess of standard iodine solution, retitrating the latter by sodium arsenite, and estimating the total sulphuric acid formed in another portion of the liquid by precipitation with $BaCl_2$. By retitration the quantity of SO_2 absorbed was found, and by subtracting this from the total sulphuric acid that of the SO_2 was obtained. Two experiments with burning Spanish cupreous pyrites, containing 48·62 per cent. of sulphur, in a glass tube in a current of air gave

	I.	II.
Sulphur obtained as SO_2 . .	88·02	80·78 per cent.
,, . SO_3 .	5·80	6·05 ,,
in the residue .	3·43	5·17 ,,
lost	2·75	

Of the sulphur of the burner-gas itself there was present—

	I.	II.
As SO_2 . . .	93·83	93·63 per cent.
„ SO_3 . . .	6·17	6·37 „

Two other experiments were made in this way:—In a glass tube 50 g. of cinders from the same pyrites, in pieces about the size of a pea, were completely freed from sulphur by ignition, and fresh pyrites was burnt as before, the gas passing through the cinders. Found:—

	III.	IV.
Sulphur as SO_2 . .	79·25	76·90 per cent.
„ SO_3 . .	16·02	16·84 „
Residue and loss . .	4·73	6·26 „

Of the sulphur of the burner-gas itself there was present:—

	III.	IV.
As SO_2 . . .	83·18	82·00 per cent.
„ SO_3 . . .	16·82	18·00 „

On the large scale the formation of SO_3 will hardly be as considerable as in the last two experiments, because in the burners the gas passes through much less ignited ferric oxide than in our experiments.

By later experiments in my laboratory (*Chem. Zeit.*, 1883, p. 29) it was found that in roasting pyrites by itself 5·05 per cent., but when passing the gases through a layer of red-hot pyrites-cinders 15·8 per cent. of the total sulphur reappeared as SO_3, which entirely confirms the above results. On burning *brimstone* it was found that even then 2·48 to 2·80 per cent. of the sulphur was converted into SO_3; and this quantity was increased to 9·5 to 13·1 per cent. if the gases were passed through red-hot pyrites-cinders.

Hempel (*Ber.*, 1890, p. 1455) found that, on burning brimstone in oxygen at the ordinary atmospheric pressure, about 2 per cent. of it was converted into SO_3 (which agrees with my results, as given above); but when effecting the combustion under a pressure of 40 or 50 atm., about 50 per cent. of the sulphur was converted into SO_3.

Further experiments were made by Scheurer-Kestner (*Bul Soc. Chim.*, xliii. p. 9; xliv. p. 98) with the gases from pyrites kilns as given off in actual manufacturing. We quote here series of his results, obtained with samples of burner-gas taken at various times—A, from a lump-burner; B, from a Malétra dust-burner.

	Volume per cent. of SO_2	Sulphur converted into SO_3 per cent of total S	
A. *Lump-burner.*	7·3	2·8	Average 3·1
	7·5	5·8	
	6·5	1·2	
	6·6	1·0	
	8·3	0·0	
	9·9	2·8	
	6·2	8·4	
B. *Dust-burner.*	8·2	3·0	Average 3·5
	9·0	6·8	
	7·6	0·4	
	11·3	0·8	
	7·7	1·0	
	8·7	2·5	
	8·7	9·3	
	7·6	4·1	

e quantity of SO_3 formed is here found to be very lar, varying from 0 to 9·3 per cent. of the SO_2; the average is decidedly less than in our laboratory experiments with pyrites.

F. Fischer (*Dingl. polyt. J.*, cclviii. p. 28) obtained the following results, which at the same time give an idea of the difference in the composition of the gases on the various shelves of a Malétra dust-burner:—

	SO_2 per cent	SO_3 per cent	O per cent.
A. *First test* (shelf-burner)			
Second shelf from below	0·96	0·44	18·4
Fourth „ „	1·52	0·68	16·6
Sixth „ „	3·81	0·97	12·5
Main flue	8·26	1·34	5·9
„ „	7·53	1·27	7·5
B. *Second test* (shelf-burner).			
Sixth shelf from below	8·43	3·17	3·9
„ „	4·92	0·68	10·7
Second shelf from below	2·48	1·42	14·8
Fourth „ „	2·62	0·78	16·0
Main flue	5·80	0·65	10·6
C. *Lump-burner* . . . up to	9·3	2·1	5·0

These tests were made by an expeditious method which cannot compete in respect of accuracy with that employed by me or by Scheurer-Kestner. The much larger quantity of SO_3 in proportion to SO_2 is perhaps explicable in this way.[1]

Blende-roasting gases, when tested by my method at the Rhenania works at Stolberg, yielded up to 25 per cent. of the total S as SO_3.

If the burner-gases are not passed hot into a Glover tower, but are cooled in the old way, most of the SO_3 condenses in the shape of sulphuric acid, more than enough water for this purpose being contained in the air and the pyrites. Where the gases go into a Glover tower, this, of course, retains all the SO_3 previously formed, also in the shape of SO_2H_4 (Scheurer-Kestner, *loc. cit.*). We shall further on consider this fact in detail when speaking of the Glover tower and the formation of sulphuric acid generally.

The constant presence of sulphuric anhydride in various proportions in the burner-gas, is, of course, a source of inaccuracy in the testing process according to Reich (see below), which indicates only the sulphur dioxide, as we shall see later on; it causes, moreover, a deficiency of oxygen and an excess of nitrogen in the composition of the gases. Hitherto no satisfactory relation has been found between the amount of SO_2, SO_3, O, and N in the many analyses of burner-gases, as is apparent from the disputes between Scheurer-Kestner and Bode (*vide suprà*, p. 564; *cf.* also *Berl. Ber.*, vii. p. 1665); as well as from Fischer's tests just quoted.

The above-mentioned results have led to the following attempt of increasing the formation of sulphur trioxide in the roasting process. Collett and Eckardt (Norw. P. 20273) increase the percentage of SO_3 in burner-gases by passing them, mixed with air in excess, over the hottest part of the burnt ore, whereby a great part of the SO_2 is converted into SO_3. Pyrites and air enter the burner, not, as otherwise usual, in opposite directions, but in parallel currents, and the gas and the hot cinders are allowed to act upon each other for a sufficiently long time. The burner-gases in that case contain so much SO_3 that they can be employed directly for the manufacture of ammonium sulphate (comp. *suprà*, p. 500).

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[1] Harpf (*Dingl. polyt. J.*, ccci. part 2) has grossly misinterpreted Scheurer-Kestner's results, as shown by me, *ibid.*, part 4.

6. *Actual Percentage of Sulphur Dioxide in Burner-gas.*

A source of dilution of the burner-gas, not easily traceable quantitatively, is this—that the burnt ore does not contain pure Fe_2O_3, but also sulphates of iron, which must always retain more oxygen than Fe_2O_3, and the nitrogen corresponding to this excess of oxygen must be found in the burner-gas. On the other hand, a little nitrogen will have to be deducted if in the burnt ore FeS is present; but this amounts to very little indeed.

Moreover, in the factories working with nitrate of soda decomposed immediately behind the burners, the dilution of gas caused thereby must be accounted for. The calculated density of NO_3H is 2·17823; we need only take this into account, as the NO_3H forms the largest portion of the gas given off by the nitre mixture. It differs so little from that of SO_2 (viz., 2·2109) that, looking at the small quantities in question, we can take the two as equal without any sensible error. Now in normal working order, and using a Gay-Lussac tower, certainly not above 5 per cent. of nitre on the burnt sulphur is consumed (corresponding to 3·7 per cent. of NO_3H), or 1·85 upon the SO_2. Thus a gaseous mixture which, without the nitric acid, contains 8·59 per cent of SO_2, contains besides $\frac{1·85 \times 8·59}{100}$ nitric acid vapour, which increases its volume to 100·1589, and diminishes the percentage of SO_2 in the total volume to 8·576—a diminution too slight to be traceable by analysis. Also if the nitric acid is not calculated as such, but as NO_2 or N_2O_3, it has no sensible influence upon the analyses, even if the sample of gas is taken in a place where the nitrous vapours coming from the Gay-Lussac tower have already entered into the process.

Still all the above-mentioned causes unite in somewhat diminishing the percentage of SO_2 in the burner-gas: so that the percentages stated above:—

11·23 per cent. by volume in burning sulphur,
8·59 „ „ „ pyrites,

must be looked upon as the *maximum*, which in practice can only be approached, but hardly ever reached, and which ought never to be exceeded.

If the sulphur dioxide in the burner-gas be estimated, this will sufficiently test the style of burning, since the oxygen of the gas must necessarily be in inverse proportion to its sulphur dioxide—although not exactly, as the sulphuric anhydride comes into play. In practice, usually from 11 to 13 per cent. of oxygen is found in good burner-gas.

The innumerable observations made upon the percentage of burner-gas in chemical works have proved that with very good pyrites the above maximum figures can be very nearly approached, whilst with other ores, badly burning or containing unfavourable metallic sulphides, only 7 to 7½ per cent. SO_2 in the burner-gas is attained (*e.g.* Buchner, *Dingl. polyt. J.*, ccxv. p. 557). Of course, looking at the difficulty of keeping the evolution of gas exactly uniform, the different observations made in the course of a day will frequently yield less than the above figures (*e.g.* Scheurer-Kestner, *ibid.*, ccxix. p. 117, in one day found 6·5, 6·5, 6·0, 8·0, 9·0, 8·7; even greater differences occur in his tests quoted *suprà*, p. 564); and they only signify the *average* percentage of the burner-gas. As a *minimum*, below which the gas of real pyrites ought never to fall, 6 per cent.—as ordinary *average*, 7 to 8 per cent. SO_2 by volume can be assumed. If less is found, the draught should be cut off; if more, more air should be admitted.

Crowder (*J. Soc. Chem. Ind.*, 1891, p. 298) quotes the following observations on the volume-percentage of burner-gas (details in the original; no account is taken of the SO_3 present):—

		SO_2.	O.
Lump-kilns	from	4·97 to 6·33	9·60 to 11·21
Old dust-kilns (shelf-burners)	„	6·03 „ 7·02	9·10 „ 10·00
„ another ore	„	6·34 „ 7·43	7·78 „ 8·82
New dust-kilns	„	4·86 „ 7·03	8·98 „ 10·68

The *temperature* of the gas, where it enters the Glover tower, in the case of lump-burners is between the melting-points of zinc (412° C.) and antimony (432°). The gas from dust-burners, which has first to traverse a series of dust-chambers, is generally hot enough to melt lead (= 326°), but it is sometimes rather less.

All the above calculations refer only to pyrites proper—that is, such as contains merely a few per cent. of other metallic sulphides. If the latter have to be roasted by themselves (for instance, preparatory to their metallurgical utilisation), only poor gas can be obtained, partly because more sulphates remain in the residue, for which the corresponding nitrogen is found in the gas, partly because they must be roasted altogether with a larger excess of air.

Bode states (*Glovertlhurm*, p. 88) that at Oker poor ores with 27 per cent. sulphur, of which only 22 per cent. was combined with iron, the remainder being present as blende and barium sulphate, yielded gas with 5·5 per cent. SO_2. Lead-matte yields gas with 5 to 5·5 per cent.; coarse copper metal (with 34 per cent. Cu, 28 per cent. Fe, and 28 per cent. S), 5·5 per cent. SO_2.

According to Wunderlich (*Z. f. d. chem." Grossgew.*, i. p. 74), the gas at Oker contains 5 to 7 per cent. SO_2; its temperature in the case of ores rich in sulphur reaches 360°, in the case of poorer ores about 230°.

In the case of the Rhenania blende-roasters (p. 504) the gases arrive at the Glover tower above 300°, sometimes up to 400° (information received in 1902).

Attention must be drawn to a circumstance frequently overlooked in analyses—that for technical purposes very rarely a reduction of the volumes of gases to 0 and 760 mm. is effected. This matters less in ordinary gas-analysis than in tests like that of Reich, where the gases are compared with a fixed quantity of SO_2 assumed to be at 0° and 760 mm. This causes most tests made by Reich's method to indicate less than the real percentage of SO_2 present.

Usually 4 per cent. SO_2 in the gases entering the chambers is considered the minimum at which it is possible to make sulphuric acid without actually losing money by the process. Locally, of course, this may be modified to some little extent. At Freiberg 4 to 3½ per cent. SO_2 is stated as the minimum at which the manufacture of sulphuric acid can be carried on without pecuniary loss. The average at those works, where a great variety of poor ores, all arsenical, and "matte" is roasted, preparatory to the smelting process, is from 5 to 7 per cent. SO_2 in the burner-gas.

Supra (p. 562) we have mentioned the assertion of Sjöstedt, according to which pyrites-burner gas can be got up to 14 vols. per cent. SO_2, for the manufacture of wood-pulp.

7. *The Quantitative Estimation of Sulphur Dioxide in Burner-gas.*

This is usually effected by Reich's process, which consists in aspirating the gas through a measured quantity of a solution of iodine, to which a little starch has been added. This is carried on till the blue colour of the solution disappears; the amount of gas aspirated in proportion to the constant quantity of iodine employed admits of calculating the percentage of SO_2 in the gas.

The reaction taking place is as follows:

$$2I + SO_2 + 2H_2O = 2HI + H_2SO_4.$$

The operation is carried on with the apparatus shown in Fig. 156. A is a wide-mouthed bottle of about 200 or 300 c.c. capacity, provided with a three-times perforated india-rubber cork. Through one perforation passes the glass tube *a*, which, by means of the elastic tube *b*, serves for introducing the gas; for this purpose a hole is drilled in some convenient part of the burner-pipe, and the india-rubber cork *c* exactly fitted into it. The second, somewhat wider perforation is closed by the small plug *d*; through the third perforation the elbow tube *e* passes, which is connected with the corresponding tube *f* of the bottle B, holding 2 or 3 l. The latter serves as an aspirator—the glass tube *g*, reaching to its bottom, being continued into an elastic tube *h* closed by the pinch-cock *i*, the whole when once filled serving as a siphon. The graduated cylinder, C, holds 250 c.c.

When the sulphur dioxide in any gaseous mixture has to be estimated, the cork *c* is inserted into a hole of the pipe conveying the gas. The vessel A is filled up to about half of its capacity, through *d*, with water; and B is filled almost entirely. A small quantity (usually 10 c.c.) of standard iodine solution (12·65 g. I in 1 l. of water) is added to the water in A, along with a little starch, by which the water assumes an intensely blue colour. The pinch-cock on the elastic tube *b* is shut so that no air can enter into A; *i* is opened, so that water runs out until the air in A and B is so far expanded that the column of water in B is supported. The water then ceases to run, provided that everything closes air-tight; if not, the water will continue to run. When the apparatus has been thus tested, *i* is shut and *b* opened; then *i* is opened so that the water runs out

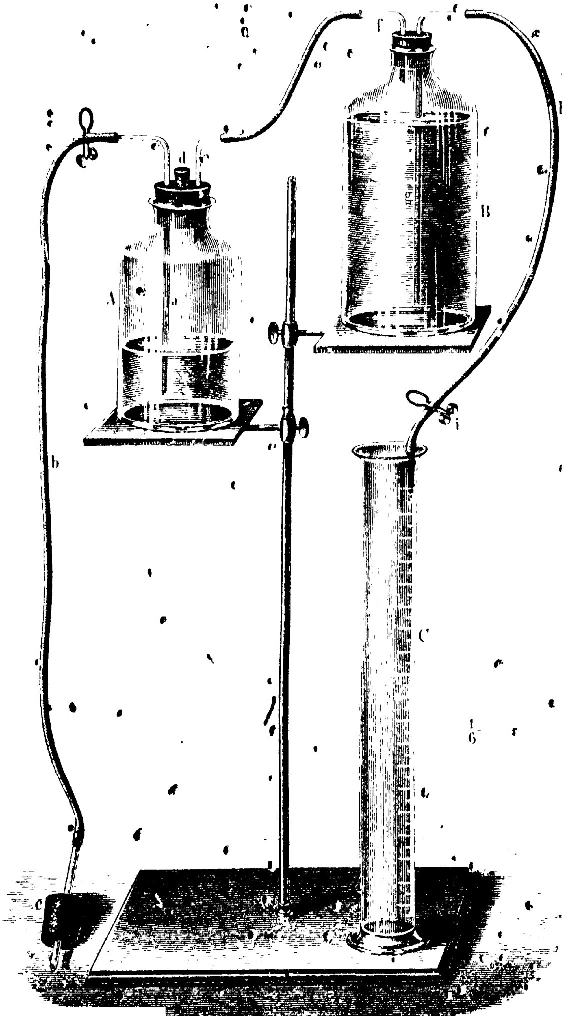

FIG. 156.

slowly, the gas to be tested entering through *a* in single bubbles and rising through the coloured water. As soon as the SO_2

contained in the gas gets into the water, it converts the free iodine into hydriodic acid; and after a certain time the liquid will be decolorised, which at last happens very suddenly and can be very accurately observed. Directly this happens, the cock i is closed. By this preliminary operation the whole of the inlet-tube is filled with the gas to be tested.

Now d is opened, and a measured volume (say, n c.c.) of standard iodine solution is put into the vessel A, by which, of course, a blue colour is again produced; d is closed again; i is cautiously opened, and water is run out till the liquid in a, which, on opening d, had risen to the level of the outer liquid, has been depressed to the point of the tube, in order to expand the gas in A up to the degree of pressure at which the following observation is made; then i is quickly shut, all the water that runs out is poured away, and the empty graduated vessel C is put back into its place. Now i is opened, and, by the running-out of the water, gas is slowly aspirated through A, till the liquid is decolorised again, whereupon i is closed, and the volume of the water run out into the graduated cylinder is measured. We will call it m c.c. In this process no sulphur dioxide escapes unabsorbed if the bottle A is constantly shaken; it is best to do this with one hand, holding the pinch-cock i open with the other hand, and letting this go the moment the colour has vanished, or even when it is but faint, as it generally disappears on shaking a little longer.

It is advisable to add to the iodine solution a little sodium bicarbonate, which will facilitate the absorption of SO_2 (C. Winkler).

If a second testing is to be made, without any further alteration a fresh quantity of iodine solution can be put in and the process recommenced. When this has been repeated a few times, the decolorised liquid in A, after a short time, again turns blue, because then its percentage of HI has become so large that it decomposes on standing and liberates iodine. This liquid must then be poured away, and replaced by fresh water and a little starch solution.

The calculation of the result is as follows:—The n c.c. of iodine solution, provided it contains 12·65 g. per litre, by its decolorisation shows 0·0032 g. SO_2, which, at 0° C., and a barometrical pressure of 760 mm., occupies a volume of $1 \cdot 114 \times n$

c.c. If the barometer shows b mm., and the thermometer t° C., and the difference of water-level in the aspirator is $= h$ mm. equal to $\frac{h}{13{\cdot}6}$ mm. of mercury, the exact volume of 0·0032 × n g. SO_2 is

$$1.114 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.003665\ t) \text{ c.c.}$$

As the water run out, and thus also the gas aspirated through A, amounts to m c.c., the volume of the aspirated gaseous mixture, before the absorption of the SO_2 contained therein, must have been

$$m + 1.114 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.003665 \times t) \text{ c.c.},$$

and the percentage of SO_2 in volumes of the gaseous mixture

$$\frac{100 \times 1.114 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.003665 \times t)}{m + 1.114 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.003665 \times t)}.$$

In many cases a correction for the barometrical and thermometrical changes will not be required; and the formula is then simply

$$\frac{111.4 \times n}{m + 1.114 \times n} \text{ per cent. } SO_2.$$

If the percentage of SO_2 in the gas is very small, and thus m very large in proportion to n, the formula may be simplified into

$$\frac{111.4 \times n}{m}$$

If 10 c.c. of a decinormal iodine solution (= 12·65 g. in 1000 c.c.) have been put into A, this quantity, according to the above-given formula, will correspond to 0·032 g., or 11·14 c.c. SO_2, at 0° C. and 760 mm.; and this number need only be multiplied by 100, and divided by the number of cubic centimetres of water collected in C, *plus* 11, in order to find the percentage of SO_2 in the gas. The barometrical and thermometrical corrections are in this case, of course, neglected. The subjoined table will save this calculation. On employing 10 c.c. of decinormal iodine solution, the following number of cubic centimetres collected in the graduated cylinder, C, show:—

Cubic centimetres.	Volume percentage of SO_2.
82	12·0
86	11·5
90	11·0
95	10·5
100	10·0
106	9·5
113	9·0
120	8·5
128	8·0
138	7·5
148	7·0
160	6·5
175	6·0
192	5·5
212	5·0

Even if the gas to be examined is taken at a point where it is already mixed with nitre gas, this will not exercise any practically important influence upon the result. We have already seen that, in ordinary work, for each 100 parts of SO_2 only 1·85 NHO_3, or its equivalent as N_2O_3 or NO_2, exists in the gas. In such dilute aqueous solutions as come into question here nitric acid hardly at all oxidises sulphurous acid; this, however, is done by nitrous and hyponitric acids. Even if we assume that only NO_2 is formed (which is going much too far), this could at most oxidise its equivalent in SO_2, according to the formula

$$NO_2 + H_2O + SO_2 = SO_4H_2 + NO.$$

46 NO_2 thus oxidises 64 SO_3, or 1·35 NO_2 (the equivalent of 1·85 NO_3H) only 1·88 SO_2; in other words, in the worst case, never happening in practical work, of 100 parts SO_2 1·88 parts would be oxidised by nitrogen acids instead of iodine. Even this maximum error would, say, at 10 per cent., only amount to

a deficiency of 0·188 per cent.; but this is certainly reckoning it much too high.

Raschig (*Z. angew. Chem.*, 1909, p. 1182) points out an inaccuracy connected with this method in consequence of the presence of nitrous gases, and the uncertainty of recognising the end of the reaction, owing to the fact that the iodine solution, after being decolorised, again takes a blue colour through the action of nitrous acid. This fault is, however, avoided, if sodium acetate is added, say for each 10 c.c. decinormal iodine solution about 10 c.c. of a cold saturated solution of sodium acetate, and the chamber gases are filtered through glass wool before reaching the iodine solution; thus only acetic acid is present in the free state, which prevents any action of nitrous acid. This acid, in fact, or its equivalent of $NO+NO_2$, can be estimated after performing the Reich test, by adding a drop of phenolphthalein and titrating with decinormal NaOH solution till the red colour appears. From the volume of soda solution consumed must be deducted 10 c.c. for the HJ formed from the 10 c.c. $\frac{1}{10}$ normal iodine, and 10 c.c. for the H_2SO_4 formed by the reaction: $SO_2+2J+2H_2O=2HJ+H_2SO_4$; the decinormal soda solution used beyond those 20 c.c. indicates nitric and nitrous acid. [This estimation is not quite correct, because the CO_2 of air (and of that contained as impurity in the NaOH solution) also acts on phenolphthalein, and no boiling out can be allowed here because then the nitrous acid would be driven out as well.]

8. *Lunge's Test for Total Acids in the Burner-gas.*

Considering the inaccuracy peculiar to Reich's test, owing to the constant presence of sulphuric anhydride in the burner-gas (cf. *suprà*, pp. 563 *et seq.*), the question arises whether it would not be better to substitute for it a test showing the *total acidity* of the burner-gases. There is no difficulty in doing this, either by the method indicated for testing the exit-gases, or in a more expeditious way by employing in the apparatus (Fig. 157) a caustic-soda solution tinged red by phenolphthalein (litmus is not suitable in this, nor is methyl-orange, which acts differently upon sulphurous and sulphuric acid, *cf.* p. 354). I have shown this method to be quite practicable and accurate, and it is carried out at many works for the regular control of the process.

A decinormal solution of caustic soda is employed, of which 10 c.c. are tinged red with phenolphthalein and diluted to about 100 or 200 c.c. The gas is aspirated through it slowly, exactly as in Reich's test, with continuous shaking. Especially towards the end the shaking must be continued for a while (say half a minute), each time aspirating a few cubic centimetres of gas through the liquid, till the colour has been completely discharged, which is best ascertained by putting a white piece of paper or the like underneath the bottle. The calculation is made exactly as with the iodine test, counting all the acids as SO_2. A large number of practical tests made in this manner have shown that the percentage of total acids calculated as SO_2 is always larger than the figures found by the iodine test, owing to the presence of SO_3, and that the results of the former test agree with those of gravimetrical estimations.

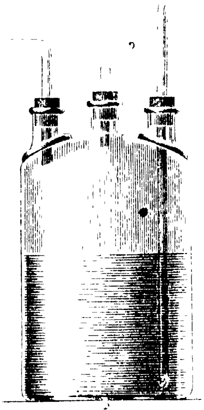

FIG. 157.

The absorption-bottle used by me differs from Reich's in having an inlet-tube for the gas, closed at the bottom, and perforated by many pin-holes, through which the gas rises in many minute bubbles, instead of one large bubble, as shown in Fig. 157. Experience proves this to be greatly superior to Fig. 156.

The otherwise excellent absorbing-bottle described in

No. 34 of the *Alkali Inspectors' Reports*, p. 22, is not available in this case, as it contains india-rubber rings, which act upon iodine.

9. *Estimation of Oxygen in Burner- and Chamber-gases.*

Although burner-gas is not generally tested for oxygen, this test being reserved for the exit-gases, we will here describe the methods employed for estimating oxygen in any of the gases occurring in the manufacture of sulphuric acid.

Oxygen is for technical purposes always estimated by means of an absorbent, observing the contraction of volume produced. Some of these absorbents are not now employed, *e.g.* nitric oxide (used by Priestley and by Scheurer-Kestner, *Comptes rend.*, lxviii. p 608; also recommended by Wanklyn), ferrous hydrate (Vogt, *Dingl. polyt. J.*, ccx. p. 103), and others. Cuprous chloride in ammoniacal solution may be employed for absorbing oxygen, but it has no advantages over pyrogallol or phosphorus, and several drawbacks, so that it cannot be recommended. The choice really lies between the two agents just mentioned.

Of these *pyrogallol* must be used in an alkaline solution, and it acts very promptly indeed. Its use for this purpose was proposed by Chevreul as early as 1820, but it became general only through Liebig many years after. It is true that this reagent in the presence of pure oxygen forms some carbon monoxide (Grace Calvert, *Proc. Manch. Lit. and Phil. Soc.*, 1863, p. 184); but this never happens with gaseous mixtures containing no more oxygen than atmospheric air (Poleck, *Z. anal. Chem.*, 1869, p. 451). It is therefore altogether reliable in the present case, and is very much employed. Unfortunately the solution (25 g. potassium hydrate and 10 g. pyrogallol to 400 c.c. water) gradually thickens and becomes useless long before this somewhat expensive reagent has been used up.

Phosphorus is one of the oldest absorbents for oxygen, and it has again come into use, since the manner of employing it has been properly studied, and as it is now found in trade in very thin sticks, offering a great surface. Of course it must be kept under water, and must be exposed only to the gas to be analysed. It acts only at a temperature of at least 16°, better a little above; this is the first condition to be observed in its use, but it is easy to attain if the apparatus is kept in a somewhat warm place (near an acid-chamber). The action of phosphorus on oxygen is interfered with by traces of tarry matters and the like; but such do not occur in chamber-gas. As it is, the gases, both for the pyrogallol and the phosphorus test, are often previously washed and freed from acids by passing them through a solution of caustic potash; but there is generally no great error caused by omitting this treatment. The action of the oxygen on the phosphorus is at once indicated by the formation of a white cloud, and it is necessary to wait a few minutes till that cloud has completely disappeared, when the absorption of oxygen will be complete. Once charged, such an apparatus may serve for hundreds of tests, but it should be kept protected from daylight.

The apparatus employed for estimating oxygen in gaseous mixtures may be of various descriptions. Those most used are Orsat's apparatus (*cf.* Lunge's *Technical Chemists' Handbook*, p. 97, and Winkler-Lunge's *Technical Gas-Analysis*, 2nd edition, p. 87), Lindemann's apparatus (*ibid.*, p. 92), and M. Liebig's apparatus (*Dingl. polyt. J.*, ccvii. p. 37, and ccxxxiii. p. 396); Younger's apparatus (*J. Soc. Chem. Ind.*, 1887, p. 348) is a slight modification of the latter. The two former can be used for phosphorus or pyrogallol, the latter for pyrogallol only.

Of course Hempel's, Bunte's, or any other apparatus for general technical gas-analysis may be employed as well.

Instead of taking only single samples of the escaping gas, it is advisable, apart from these, to collect an average sample (say, for twenty-four hours) by aspirating a certain quantity (say, about 50 l.) by means of a large aspirator with the outlet-cock very slightly opened. Owing to the slowness of the aspiration, the gas standing over the water in the aspirator will be thoroughly mixed up, and by taking a sample from the aspirator the *average* percentage of oxygen can be estimated with some degree of accuracy. We shall treat this matter more in detail in Chapter VII., when describing the testing of the exit-gases.

10. *Estimation of the Oxides and Acids of Nitrogen in Gaseous Mixtures.*

Burner-gas will contain the above acids if the "potting" has been done either within or close to the burners, as is usual in England. The acids and oxides of nitrogen are, however, but exceptionally estimated in burner-gas, and not very often even in chamber-gas; the latter is not indispensable, because the colour of the chamber-gas on the one hand, and the testing of the "drips" on the other, which we shall describe in Chapter V., are sufficient for guiding the manufacturer in his work.

In well-conducted works, however, the chamber-exits are tested not merely for total acidity, but also for nitrogen acids separately. For this purpose the prescriptions formulated by the British Alkali-Makers' Association may be observed, which we shall give in detail later on (Chapter VII.). These do not extend to nitric oxide, but we shall see that it is easy to estimate this at the same time. In this place we shall give a short outline of the methods employed by Lunge and Naef for their extended experimental investigation of the vitriol-chamber process (*Chem. Ind.*, 1884, p. 5) for *estimating nitrogen oxides and sulphur dioxide at the same time.* The pipe bringing the gas from the chambers is continued into a Y-pipe, both branches of which are connected with sets of absorbing-tubes. One branch is connected with three U-tubes containing concentrated pure sulphuric acid (for retaining N_2O_3 and N_2O_4) and a fourth tube containing an acidulated solution of potassium permanganate (for retaining NO). The other branch of the Y-pipe first leads into a long glass tube filled with cotton-wool or glass-wool, where any drops of mechanically carried-over sulphuric acid are retained, and then into two U-tubes containing pure caustic-soda solution (for estimating SO_2). At the end of both sets of tubes there is an aspirator, consisting of a large glass bottle, holding about 20 l., divided into single litres, with a tap or tap-siphon leading into a similar bottle, so that the quantity of water run out indicates the quantity of gas passed through each set of tubes. The gas remaining in the aspirators is tested for *oxygen* by absorption; *nitrogen* by difference. *Sulphur dioxide* is found by oxidising the caustic-soda solution with bromine water, and precipitating the sulphuric acid formed by barium chloride. In the sulphuric acid *nitrogen trioxide* and *tetroxide* are estimated in the way indicated in Chapter III (p. 378 *et seq.*), by testing both with permanganate and with the nitrometer. The tube filled with potassium permanganate must have retained the *nitric oxide* which is found by adding titrated ferrous sulphate solution and retitrating with permanganate. Where the quantity of SO_2 in the gas is considerable, this method cannot be employed; in this case it is not possible to separate the N_2O_3 and N_2O_4, and the method otherwise used for the chamber-exits must be employed (Chapter VII.).

Nitrogen protoxide, N_2O, may occur in chamber-gases in very slight quantities. The former methods of its detection and estimation were very inadequate and failed entirely in the presence of other nitrogen oxides. It may be possible to apply the method proposed by Knorre (*Berl. Ber.*, xxxiii. p. 2136), viz., burning with excess of hydrogen in a Drehschmidt's platinum capillary (*cf.* Winkler-Lunge's *Technical Gas-Analysis*, 2nd edition, p. 162), or else Pollak's method (described in his inaugural dissertation, *Prag*, 1902, p. 52, and in Treadwell's *Lehrbuch der anal. Chem.*, 2nd edition, ii. p. 538) of burning in a bright red-hot Drehschmidt's capillary with pure carbon monoxide, measuring the contraction and estimating the CO_2 formed. The contraction in burning for NO is $\frac{NO}{2}$; for N_2O there is no contraction at all; the volume of the absorbed CO_2 is equal to $NO + N_2O$. Hence the volume of N_2O is obtained by deducting twice the volume of the first contraction from the volume of CO found. This is made clear by the following equations:—

$$2 \text{ vol. } NO + 2 \text{ vol. } CO = 1 \text{ vol. } N_2 + 2 \text{ vol. } CO_2.$$
$$1 \text{ vol. } N_2O + 1 \text{ vol. } CO = 1 \text{ vol. } N_2 + 1 \text{ vol. } CO_2.$$

Hempel (*Z. Elektrochem.*, 1906, pp. 600 *et seq.*) estimates very slight quantities of nitrogen protoxide, such as may be suspected in chamber-gases, by cooling the gases by means of liquid air, which causes the N_2O to condense to a liquid, adding to it electrolytic fulminating-gas ($H_2 + O$) and exploding in an explosion-pipette. The increase of the volume of the gas thus produced corresponds to half the N_2O originally present. He thus found in the exit-gases from the Freiberg factory, 0·063 to 0·073 per cent.; from the Aussig factory, 0·11 to 0·14 per cent.; in a very bad chamber-gas, 0·25 per cent. N_2O.

END OF PART I.

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CHAPTER III

THE PROPERTIES AND ANALYSIS OF THE TECHNICALLY EMPLOYED OXIDES AND ACIDS OF SULPHUR

Sesquioxide of Sulphur, S_2O_3.

This substance, the anhydride of thiosulphuric acid, is obtained by dissolving sulphur in fuming oil of vitriol. According to Witt (*Chem. Ind. d. deutsch. Reiches*, p. 118), it is preferable to all other agents as a reducing agent (dissolved in sulphuric acid) in the manufacture of naphtazarin and several other cases.

Sulphur Dioxide, SO_2. (Sulphurous Anhydride.)

Sulphur dioxide is at the ordinary temperature and pressure a colourless gas of suffocating smell, neither supporting combustion nor combustible itself directly. Even when greatly diluted with air it has a very injurious action upon plants and animals (*cf.* further on, pp. 268 *et seq.*).

Sulphur dioxide contains 50·05 per cent. by weight of sulphur and 49·95 per cent. oxygen. Molecular weight 64·06 (O = 16). Its specific gravity has been found by various observers = 2·222 to 2·247 (air = 1); calculated from the molecular weight = 2·2136. A litre of the gas at 0° C. and 760 mm. pressure weighs 2·8608 g. Its coefficient of dilatation is not exactly equal to that of air, but rather larger, especially at lower temperatures, namely for each 1° C., according to Amagat:—

Degrees.	
Between 0 and 10	0·004233
„ 10 „ 20	0·004005
At 50	0·003846
„ 100	0·003757
„ 150	0·003718
„ 200	0·003695
„ 250	0·003685

Its specific heat, compared with its equal weight of water is =0·1544; compared with its equal weight of air =0·3414. Mathias (*Comptes rend.*, cxix. p. 404) gives it as between −20° and +130° C.:

$$0·31712 + 0·0003507t + 0·000006762t^2.$$

The density of *saturated* vapour of SO_2 (that is, in contact with liquid SO_2) at various temperatures (water of 0° = 1) is, according to Cailletet and Mathias (*Comptes rend.*, civ. p. 1536):—

Cent.			Cent.		
At 7·3	.	0·00624	At 100·6	.	0·0786
,, 16·5	.	0·00858	,, 123	.	0·1340
,, 24·7	.	0·0112	,, 130	.	0·1607
,, 37·5	.	0·0169	,, 135	.	0·1888
,, 45·4	.	0·0218	,, 144	.	0·2195
,, 58·2	.	0·0310	,, 152·5	.	0·3426
,, 78·7	.	0·0464	,, 154·9	.	0·4017
,, 91·0	.	0·0626	,, 156	critical point.	

The heat of formation of 1 g.-mol. of SO_2 (=64·06) from ordinary (rhombical) sulphur is = 71,080 cal. (Thomsen), or 69,260 cal. (Berthelot).

By moderate cooling sulphur dioxide can be condensed to a *liquid*, even without application of pressure. Liquid SO_2 is a colourless mobile fluid, of about the same refractive power as water, boiling at −10° C. (Gibbs, *J. Amer. Chem. Soc.*, 1905, p. 851, found the boiling-point of dry SO_2 at 760 mm. pressure equals −10°·09); but on drawing it off at the ordinary temperature from a reservoir it remains liquid for some time, the evaporation cooling it down below its boiling-point. Its latent heat at 0° is 91·2, at 10° 88·7, at 20° 84·7, at 30° 80·5.

Its vapour-tension is:—

At 0 = 0·53 atmosphere overpressure
,, 10 = 1·26 ,, ,,
,, 20 = 2·24 atmospheres ,,
,, 30 = 3·51 ,, ,,
,, 40 = 5·15 ,, ,,

The specific gravity of liquid sulphur dioxide at various temperatures has been accurately determined by A. Lange (*J. angew. Chem.*, 1899, p. 275) as follows:—

Temperature.	Specific gravity.	Temperature.	Specific gravity.
- 20° C.	1·4846	+ 20° C.	1·3831
- 10°	1·4601	25°	1·3695
- 5°	1·4476	30°	1·3556
0°	1·4350	35°	1·3441
+ 5°	1·4223	40°	1·3264
10°	1·4095	50°	1·2957
15°	1·3964	60°	1·2633

He found that absolutely anhydrous liquid sulphur dioxide does not act upon iron up to 100° C. Technical sulphur dioxide has a slight action, owing to the presence of a little water. The temperature at which this takes place increases with the purity of the acid, *e.g.* it is 70° in the case of acid containing 0·7 per cent. H_2O. Since liquid SO_2 cannot dissolve more than 1 per cent. water, even the most impure product cannot act on the iron vessels in which it is transported at ordinary temperatures. The mixture of ferrous sulphite and thiosulphate formed, moreover, acts as a protecting crust. In ice-machines where SO_2 is the active agent, and where the temperature in the pumps may rise considerably, only absolutely anhydrous SO_2 should be employed. (*Cf.*, on this subject, also, *Z. angew. Chem.*, 1899, pp. 300 and 595.)

Production.—Sulphur dioxide is produced by burning brimstone, and by heating (roasting) many metallic sulphides, in the presence of air; by the action of strong mineral acids, both on its own salts, the sulphites, and on the thiosulphates and all polythionic acids; by heating sulphuric anhydride with sulphur, or by heating oil of vitriol with brimstone, coal, organic substances, or several metals; by strongly heating the vapour of sulphuric anhydride, or sulphuric acid, with simultaneous formation of oxygen and water respectively; and by igniting many sulphates, whereby the sulphuric anhydride first liberated at once splits up into sulphur dioxide and oxygen.

According to Scott, when sulphur dioxide (mixed with CO_2) is to be made by the process mostly used on the small or moderately small scale, *viz.*, that of heating sulphuric acid with charcoal, it is best to employ acid of 74 per cent. SO_3 = 165° Tw. If stronger acid be used, a portion of it is reduced to sulphur, which may produce iron sulphide with the iron of the apparatus; with weaker acid sulphuretted hydrogen is formed. In order to obtain the gas as pure as possible, the washing-water should be mixed with lead sulphate or coarsely-powdered charcoal.

Thus sulphur dioxide is produced from sulphuric acid or anhydride in many ways by reductive processes. On the other hand, the sulphur dioxide passes over, even more easily, into sulphuric acid by oxidation processes; and it is accordingly one of the most frequent and potent reducing agents. Under certain conditions, by the action of light, of the electric current, or of a very high temperature and pressure combined, sulphur dioxide splits up into sulphur and sulphuric anhydride. In the presence of oxygen (for instance, that of atmospheric air), or of bodies easily parting with their oxygen (such as the higher oxides of nitrogen, of manganese, of lead), sulphuric acid or its salts are formed. A very important reaction is that between SO_2 and sulphuretted hydrogen, H_2S. When completely dry the two gases do not seem to act upon each other. Even in the presence of moisture no action takes place at temperatures above 400° C. (E. Mulder). At the ordinary temperature water and sulphur are produced, but at the same time also pentathionic acid, according to the equation:

$$5SO_2 + 5H_2S = S_5O_6H_2 + 4H_2O + 5S.$$

This action occurs simultaneously with the simple reaction:

$$SO_2 + 2H_2S = 2H_2O + S_3,$$

one or the other of these prevailing, according to the proportion of the two gases in the mixture.

Behaviour of SO_2 *towards Water.*—Sulphur dioxide does not take up just 1 mol. of H_2O to form sulphurous acid proper, SO_3H_2, but under certain conditions it yields a solid compound with much more water (9, 11, or 15 H_2O to SO_2), which has not yet been definitely investigated. Sulphur dioxide dissolves pretty freely in water; and this solution behaves in every way as if it contained the real acid SO_3H_2; but constantly, even at the ordinary temperature, the dioxide (SO_2) evaporates from it. One volume of water absorbs, under 760 mm. pressure and at 0°, nearly 80 vols. SO_2. The coefficient of absorption, according to Bunsen and Schönfeld, at temperatures ranging between 0° and 20°, is

$$79.789 - 2.6077t + 0.029349t^2;$$

at temperatures between 21° and 40°,

$$75.182 - 2.1716t + 0.01903t^2.$$

The saturated acid contains at 0° 68·861 vols. of gaseous SO_2, and has a sp. gr. of 1·06091; at 10° it contains 51·383 vols. gaseous SO_2, and has the sp. gr. 1·05472; at 20°, 36·206 vols. SO_2, sp. gr. 1·02386. The absorbed gas does not escape on freezing; on boiling a long time it goes away completely. Alcohol absorbs a much larger form of sulphur dioxide (at 0° and 0·76 m. pressure, 338·62 vols. SO_2.

From Bunsen and Schonfeld's determinations Harpf (*Chem. Zeit.*, 1905, p. 136) calculated the following table (for normal atmospheric pressure):—

Temperature Degrees.	1 lit. water dissolves lit. SO_2.	1 lit. water dissolves grammes SO_2.	1 lit. saturated aqueous solution contains lit. SO_2	Specific gravity of aqueous solution	Per cent. SO_2 by weight in the aqueous solution.
0	79·8	228·3	68·86	1·0609	18·58
5	57·5	193·1	59·82	1·059	16·19
10	56·6	161·9	51·38	1·0547	13·93
15	47·3	135·3	43·56	1·042	11·92
20	39·4	112·7	36·21	1·0239	10·12

A table, not very much deviating from the above statements, of the solubility of sulphur dioxide in water at 0·76 m. mercurial pressure at different temperatures, is given in Kopp and Will's *Jahresber.* for 1861, p. 54.

Giles and Shearer (*J. Soc. Chem. Ind.*, 1885, p. 305) give the following table of the percentage of SO_2 in solutions of various specific gravities:—

Temperature.	Specific gravity.	Per cent. SO_2.	Temperature.	Specific gravity.	Per cent SO_2
15°·5 C.	1·0051	0·99	15°·5 C.	1·0399	8·08
15°·5 „	1·0102	2·05	15°·5 „	1·0438	8·68
15°·5 „	1·0148	2·87	15°·5 „	1·0492	9·80
15°·5 „	1·0204	4·04	15°·5 „	1·0541	10·75
15°·5 „	1·0252	4·99	12°·5	1·0597	11·65
15°·5 „	1·0297	5·89	11°·0	1·0668	13·09
15°·5 „	1·0353	7·01			

Another table, for the temperature 15° C., is given by Scott (*Pharm. Soc. J. and Trans.*, xi. p. 217):—

Per cent. SO_2.	Specific gravity.	Per cent. SO_2.	Specific gravity.
0·5	1·0028	5·5	1·0302
1·0	1·0056	6·0	1·0328
1·5	1·0085	6·5	1·0353
2·0	1·0113	7·0	1·0377
2·5	1·0141	7·5	1·0401
3·0	1·0168	8·0	1·0426
3·5	1·0194	8·5	1·0450
4·0	1·0221	9·0	1·0474
4·5	1·0248	9·5	1·0497
5·0	1·0275	10·0	1·0520

Much higher are the figures given by Pellet (*J. Soc. Chem. Ind.*, 1902, p. 171):—

Per cent SO_2 in 100 H_2O.	1.	2.	3.	4.	5.	6.
Sp. gr. at 15° to 17° C.	1·0075	1·015	1·0225	1·030	1·0375	1·045.

An apparatus for the production of aqueous solutions of sulphurous acid has been described by Holzhausel (Ger. P. 49194).

In the presence of oxygen solutions of sulphurous acid are partly converted into sulphuric acid.

Salts.—Sulphurous acid forms two series of salts (sulphites)—saturated or normal sulphites, SO_3M_2; and acid sulphites, SO_3MH, isomorphous with the corresponding carbonates.

Sulphur dioxide is absorbed by anhydrous barium oxide at 200°, better at 230°; by strontium oxide at 230°, better at 290°; in both cases the normal sulphite is formed. Calcium oxide forms at 400° a basic sulphite, $Ca_6S_5O_{16}$, which at 500° splits up into sulphate and sulphide. Magnesia absorbs SO_2 very slowly at 326°, and slightly above this the sulphate is formed (Birnbaum and Wittich, *Ber.*, 1880, p. 651).

The reactions taking place between sulphur dioxide and the oxides and acids of nitrogen will be described in a later part of this chapter.

Injurious Action of Sulphurous Acid (Sulphur Dioxide) or Animal and Vegetable Organisms.—Ogata (*Arch. f. Hygiene*, 1884, p. 223) found that 0·04 per cent. SO_2 causes difficulty of breathing after a few hours; he could not take a single full breath in air containing 0·05 per cent. SO_2. It is an acute blood-poison.

Lehmann (*Z. angew. Chem.*, 1893, p. 612) showed that persons not habituated to sulphurous acid are very little affected by 0·012 per ml., but perceptibly so by 0·015 per ml. SO_2. The presence of 0·030 per ml. after a few minutes causes strong irritation of the nasal membranes, sneezing, and slight coughing, which symptoms decrease after ten minutes. The employés and workmen accustomed to it are but little affected by 0·037 per ml.; the sensibility to SO_2 seems to be lessened by habitually respiring air containing it.

Sulphur dioxide is also very injurious to vegetation, and is one of the chief constituents of the "noxious vapours" so much complained of in most manufacturing districts. It is true that these vapours contain other injurious constituents, chiefly of an acid character, viz., sulphuric anhydride, hydrogen chloride, and sometimes even the acids of nitrogen. Disregarding the latter, and even hydrogen chloride, which will be treated of in the chapter devoted to that subject, we shall now enter upon a description of the effects produced by the ordinary "acid smoke" of metallurgical and similar works, where SO_2, and generally also SO_3, are the principal compounds to be blamed for the injurious action exercised by the smoke.

A detailed investigation of the influence of the noxious vapours at Freiberg, where very large and numerous smelting-works are situated, on vegetation and on the health of domestic animals has been made by Freytag (abstracted in Wagner's *Jahresber.*, 1873, p. 180). The acid, arsenic, and zinc vapours of the Freiberg smelting-works under favourable circumstances, even with the then existing condensing arrangements, may injure the vegetation of the neighbourhood in the following way: at a sufficient concentration they are taken up by the leaves when covered with dew; on the evaporation of the water the organs affected are corroded and reduced to the same state as that which they assume when vegetation ceases. This injury can always be proved both by the eye and by chemical analysis. A "poisoning" of the soil or of the whole plant is out of the question. The sometimes entertained assumption of an *invisible* injury done to the vegetation by the smelting-works' vapours and the awarding of damages founded thereon are unwarranted; they contradict the fundamental principles of all exact investigation and foster the desire of the unreasoning multitude to incessantly raise fresh claims for damage alleged to have been done by the works. A decrease of the nutritive value of food-plants, in cases of visible injury done to the leaves, can only occur in consequence of the loss of these leaves and the lessened ability of the plants to decompose carbonic acid and produce organic matter therefrom. Any metallic oxides or salts adhering to the leaves of food-plants may become dangerous to the animal organisation by causing inflammation of the mucous membranes, and, under very unfavourable circumstances, may produce death; but this fact can always be established with certainty by *post-mortem* examination and by chemical analysis. The supposition that the "acid disease" and tuberculosis occurring in a particular neighbourhood among the cattle are produced by the noxious vapours from smelting-works is utterly unfounded and must be most emphatically contradicted. Freytag considers that air containing more than 0·003 vol. per cent. of SO_2 will do injury to vegetation.

Schroeder (Wagner's *Jahresber.*, 1874, p. 277) made extensive experiments on the influence especially of sulphur dioxide on vegetation, with the following principal results:—From air containing as little as $\frac{1}{5000}$ of its volume of SO_2 this gas is taken up by the leaves of "leafy" (deciduous) trees and conifers; these retain it mostly, a smaller portion penetrating into the wood, the bark, and the leaf-stalks, either as such or after oxidation to sulphuric acid. Conifer leaves absorb less sulphur dioxide from the air for an equal surface of leaves than deciduous trees; the absorption takes place equally over the whole surface of the leaf, not by the stomata, and therefore has no relation to the number of the latter. A principal effect of the injurious action of sulphur dioxide is its causing a check to the normal evaporation of water, the disturbance being in a direct ratio to the quantity of SO_2; the evaporation is mostly affected by absorption of SO_2 in sunlight, at a high temperature and in dry air. The transpiration of conifers is not visibly lowered by the same quantity of sulphur dioxide as that which affects deciduous trees. The injury done by sulphur dioxide is greater if the absorption takes place at the lower than if at the upper side of the leaf.

Other communications on this subject, partly contradicting those of Schroeder, have been made by Stöckhart (Wagner's *Jahresber.*, 1874, p. 228). According to his observations at

Zwickau, a distance of 630 m. (=690 yd.) protects even the most sensitive vegetation against the effect of large volumes of vapours, if they escape through chimneys not less than 82 ft. high. Conifers are much more sensitive than deciduous trees; the decreasing series of sensibility is—pine, pitch-pine, Scotch fir, larch, hawthorn, white beech, birch, fruit-trees, hazel-nut, horse-chestnut, oak, red beech, ash, linden, maple, poplar, alder, mountain-ash. In the parts of plants corroded by sulphurous acid, not this acid, but sulphuric acid can be found, and that to a larger extent than in the same parts of plants collected at the same time in districts free from smoke.

Schroeder and Schertel (Wagner's *Jahresber.*, 1879, p. 234) found in healthy fir-leaves 0·162 to 0·237 per cent. sulphuric acid (SO_3); damage was only done when the percentage rose above 0·250; the highest found was 0·592 near Freiberg, 1·33 in the Oberharz.

Other figures given by Fricke (*Chem. Ind.*, 1887, p. 492) state the difference in the amount of sulphuric acid found in healthy and damaged plants as follows:—

	Healthy.	Damaged.
Beans	6·119	6·551
Buckwheat . . .	5·110	5·880
Grass	7·105	8·336
Rye	3·684	5·610
Wheat	2·179	4·412
Cabbage . . .	27·290	30·843
Oats	2·926	6·788
Potatoes . . .	13·000	17·500

In most cases the differences are too slight to base any trustworthy conclusions on them. Oats, wheat, and potatoes stand the acid gases better than young meadow-plants.

Just and Hiene (*Chem. Ind.*, 1889, p. 252) also found very varying percentages of sulphuric acid in plants alleged to be damaged by SO_2, so that this means of tracing such injury is very unreliable.

F. Fischer, in the 220th volume of *Dingl. polyt. J.*, p. 88, has given a short synopsis of the researches made in this direction up to 1878. A special treatise (in German) has been published on acid smoke by Hering (Cotta, 1888).

Morren (*Chem. Trade J.*, ii. p. 188) shows that leaves are more sensitive than flowers to sulphur dioxide. When this is present in a proportion of 1 part to 80,000 parts of air, the leaves of fruit-trees are visibly affected in three to five hours, and this effect seems to spread after direct action of the gas ceases. Adult leaves are usually more sensitive than young leaves. The nerves are least affected and usually remain green. Sulphurous acid dissolved in water is almost without effect on the upper surface, whilst on the lower surface each little drop causes the formation of a spot visible on both surfaces. This solution is not quickly changed into sulphuric acid; the effect of the latter is quite different from that of sulphurous acid.

Koenig (*Dingl. polyt. J.*, ccxxix. p. 299) describes the appearance of trees destroyed by the vapours from roasting blende.

Hasenclever (*Chem. Ind.*, 1879, p. 225) gives coloured and photolithographic illustrations of the ravages caused by acid vapours and metallic sulphates upon the leaves of plants and plantations of trees, side by side with those caused by frost, autumnal decay, fungi, drought, overgrowth of other trees, etc., which closely resemble the phenomena produced by the acid vapours from chemical works, and hence are frequently wrongly attributed to the latter cause. Neither is the estimation of sulphates and chlorides in the damaged leaves, etc., at all a safe guide to the detection of the real cause, looking at the enormous quantity of acids sent into the air wherever coal is consumed on a large scale. At Stolberg, near Aachen, on a superficial area of 1600 acres, 220 chimneys daily emit 34½ tons of sulphur dioxide from coal, and nearly 51 tons of SO_2 from zinc-works, glass-works, etc., the sulphuric acid and alkali-works adding only ½ ton (more correctly 480 kg.) of SO_2, and ¾ ton of HCl. Hence alkali-makers ought not to be saddled with the whole, or even the chief part, of the damage observed in the neighbourhood.

An important paper on the subject in question has been published by Hamburger (*J. Soc. Chem. Ind.*, 1884, p. 202). His conclusions, founded upon a large number of analyses of damaged leaves, are practically the same as Hasenclever's, namely, that undoubtedly injury is done to vegetation by the acids in the smoke; but much difficulty exists as to proving this with certainty in special cases, and at all events the SO_2 contained in ordinary coal-smoke contributes very largely to the injurious action popularly attributed to the emanations from chemical works.

A professional forester, Reuss, partly by himself and partly together with Schroeder, has embodied the results of laborious work on this subject in several German publications. Their conclusions have been attacked by another forester, Borggreve, but Hasenclever (*Chem. Ind.*, 1895, p. 496) has shown many mistakes in that criticism. They all agree in the conclusion that the growth of trees is only impeded by acid vapours if *visible* damage is done to the leaves. When the leaves or needles remain green, chemical analysis may prove an action of acid gases, but no real damage.

Winkler (*Z. angew. Chem.*, 1896, p. 371) ascribes the effect of noxious vapours from brick-kilns, etc., principally to their containing aqueous vapour, which, on cooling, causes the condensation of sulphurous and hydrochloric acid.

Further papers on noxious vapours, with details as to their action, are those by Hagen (*Chem. Zeit.*, 1896, p. 238), Ost (*ibid.*, 1896, p. 165), Nissenson and Neumann (*Berg u. Hütten. Zeit*, 1896, p. 145), Schroeder and Schmitz-Dumont (*Dingl. polyt. J.*, ccc. p. 65), Ost and Wehmer (*Chem. Ind.*, 1899, p. 233), Seydler (*Fischer's Jahresber.*, 1899, p. 358), Ramann and Sorauer (*ibid.*, 1900, p. 332), Wislicenus (*Z. angew. Chem.*, 1901, p. 689), Ost (*ibid.*, 1907, p. 1689), Wieler (*Fischer's Jahresber.*, 1905, p. 394, and *Chem. Zeit.*, 1908, p. 868), Sorauer (*ibid.*, p. 395), Baskerville (*Chem. Zeit.*, 1908, p. 54a).

A book, comprising the whole of this subject, has been published in 1903 by Haselhoff and Lindau, under the title: *Die Beschädigung der Vegetation durch Rauch*, another by Professor A. Wieler, *Einwirkung von Schwefliger Saure auf Pflanzen*, in 1905 (Berlin, Bornträger).

Detection and Estimation of Sulphurous Acid and Sulphur Dioxide.

Qualitative Reactions of Sulphurous Acid.—The sense of smell is a very good means for detecting the presence of SO_2, when other odorous acids are absent. Gaseous mixtures containing SO_2 together with such acids are best passed through an absorbent, *e.g.* sodium carbonate, with which afterwards the ordinary reactions for SO_2 are made. When passing such gaseous mixtures through a solution of potassium permanganate, or of iodine in potassium iodide, these liquids are decolorised, the iodine being reduced to HI. This last reaction may also be utilised on test-paper. On the other hand, a test-paper, soaked in a solution prepared by boiling 2 g. wheat-starch with 100 c.c. of water, and adding 0·2 g. of potassium iodate dissolved in 5 c.c. water, is turned blue by SO_2, by the formation of free iodine. These reactions may also be utilised for recognising the presence of SO_2 when set free from its salts by the action of sulphuric acid. One of the best reactions, specially adapted for discovering SO_2 in sulphuric acid itself, is its conversion into H_2S by means of pure zinc, or, preferably, aluminium in an acid solution. The H_2S is then recognised by its reaction on lead paper, or by the purple colour produced in an ammoniacal solution of sodium nitroprusside.

A solution of a sulphite, either neutral or with addition of some sodium bicarbonate (*just* acidulated with acetic acid), when poured into a solution of zinc sulphate containing a little sodium nitroprusside, produces a red colour or precipitate, either at once or, if very little SO_2 is present, after adding some potassium ferricyanide. This reaction is not given by thiosulphates, which are, moreover, distinguished from sulphites by their giving (generally only after a little time) a precipitate of sulphur on being treated with a stronger acid. According to Reinsch, SO_2 can be detected by boiling the acid solution with a strip of clean copper, which is thereby blackened. This is caused by the formation of cupric sulphide, and the colour is not changed by heating the strip in a glass tube; but when the colour is produced by arsenic, there is a sublimate of white arsenious acid formed in the tube.

According to Schützenberger, sulphurous acid contained in a solution can be recognised by adding a drop of indigo solution and agitating with a zinc rod; owing to the formation of hyposulphurous acid (Schützenberger's "hydrosulphuric" acid), HSO_2, the blue colour will be destroyed, but will quickly reappear in contact with the air.

The *quantitative estimation* of sulphurous acid in the free state can be performed either as will be described in the case of sulphites, or by titration with standard alkali. In the latter case, however, it must be noted that the point of neutrality is reached with phenolphthalein as indicator when the normal salt, Na_2SO_3, has been formed, so that each cubic centimetre of normal alkali (containing 0·031 NaOH) indicates 0·003203 SO_2. Of course, as is always the case with phenolphthalein, the standard alkali must be soda or potash, ammonia being useless for this purpose. But when employing methyl-orange as indicator, the point of neutrality is reached exactly at the formation of $NaHSO_3$, so that each cubic centimetre of normal alkali indicates 0·06406 SO_2. Litmus gives somewhat uncertain results, and is therefore useless as an indicator. It is thus possible to estimate free SO_2 in the presence of stronger free acids in this way: one portion of the liquid is titrated with methyl-orange, and another with phenolphthalein as indicator; in the latter case more alkali will be used, and the difference of cubic centimetres of normal alkali, multiplied by 0·06406, shows the quantity of free SO_2 present (Lunge, *J Soc. Chem. Ind.*, 1883, p. 513; Thomson, *Chem. News*, xlvii. p. 130; Blarez, in *Comptes rend.*, ciii. p 69, adduces nothing new).

The acid sulphites are neutral to methyl-orange, which consequently enables us to estimate any SO_2 present over and above $NaHSO_3$. The SO_2 present in the $NaHSO_3$ itself can be titrated with normal soda and phenolphthalein, each cubic centimetre of normal alkali indicating 0·06406 SO_2. Normal sulphites, like Na_2SO_3, can be titrated by means of methyl-orange and standard hydrochloric or sulphuric acid, the red colour appearing when $NaHSO_3$ has been formed, so that each cubic centimetre of standard acid indicates 0·06406 SO_2.

Other methods of estimating SO_2 either in the free state or in its salts are based on its reducing properties. The reagents serving for this purpose are either a standard solution of iodine or one of potassium permanganate, both of which are well known and require no description here. A decinormal solution of either indicates per cubic centimetre 0·003203 g. SO_2. The method to be recommended for testing gaseous SO_2 in burner-gas will be described when treating of that gas in Chapter IV. Special attention must be drawn to the necessity of employing water *free from air* in estimating SO_2. This is not necessary if the solution of the sulphite or sulphurous acid is run into the solution of iodine (Giles and Shearer, *J. Soc. Chem. Ind.*, 1884, p. 197, and 1885, p. 303).

In many cases the quantitative estimation of sulphurous acid can take place by converting it into sulphuric acid by means of oxidising agents: chlorine, bromine, iodine, hydrogen peroxide, etc. The sulphuric acid is then estimated in the usual way.

Sulphur dioxide in the presence of hydrogen sulphide, which gases may exist together in a state of great dilution by inert gases (as in the exit-gases from "Claus kilns"), can be estimated by passing the gases through a solution of I in KI, followed by a solution of caustic soda or, preferably, sodium thiosulphate. The iodine oxidises H_2S into $H_2O + S$, and SO_2 into H_2SO_4; hence the acidity of the solution is not affected by H_2S, merely by SO_2. On the other hand, each cubic centimetre of decinormal iodine indicates 0·003203 g. of sulphur in either case, so that the difference between the iodometrical and the alkalimetrical test gives the H_2S present. The addition of a tube with sodium thiosulphate solution is necessary, because the gaseous current carries away some iodine which is retained in that solution; the latter, before titrating the iodine solution back, is added to it (details in Lunge's paper, *J. Soc. Chem. Ind.*, November 1890).

Applications of Sulphurous Acid (Sulphur dioxide).

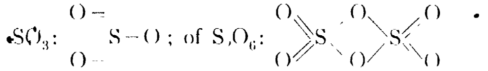
The greatest quantity of SO_2 is produced for the manufacture of sulphuric acid. Next to this in importance comes its use for the manufacture of wood-pulp, mostly in the state of calcium bisulphite (or a solution of $CaSO_3$ in an excess of sulphurous acid). One of the oldest uses of sulphur dioxide, in the shape of burning sulphur, is that as a disinfecting and antiseptic agent. For the former purpose it is not so much valued now as formerly, since it has been shown that many of the disease-germs resist the action of SO_2 for a long time. The antiseptic function of SO_2 comes into play in the fumigation of wine-casks, in the arresting of the fermentation of wort, in the manufacture of glue (where it acts also as a bleaching agent), and in many other cases.

In the textile industries sulphurous acid is largely used as a bleaching agent, especially for wool, silk, straw, etc. It is not quite certain in which way it acts in this case, possibly by forming a compound with the colouring-matters contained in the fibres. Formerly it was generally assumed that the SO_2 in bleaching acted as a reducing agent, which indeed must be true in some cases, although probably not in all. The reducing functions of SO_2 are utilised in chemical and metallurgical operations in too many cases to be enumerated here.

SULPHURIC ANHYDRIDE, SO_3
(Sulphur Trioxide),

consists of 40·05 per cent. by weight of sulphur, and 59·95 per cent. of oxygen; molecular weight, 80·06. According to Marignac (*Arch. Sci. Phys. Nat.*, xxii. p. 225, 1853; lii. p. 236, 1875; lviii. p. 228, 1877) and Schultz-Sellack (*Berl. Ber.*, iii. p. 215), it exists in two different modifications, a liquid and a solid. The liquid, α-anhydride, melts at +16° C., and begins to boil at +35° (according to Schultz-Sellack, at 46°). Specific gravity at 13° = 1·9546, at +20° (melted) = 1·97. In the melted state it is less oily than oil of vitriol, and, if pure, colourless, but usually coloured brown by dust. When kept for some time at the ordinary temperature (below 25°) it is changed into the solid β-anhydride, whose melting-point is stated very differently, from 50° to 100° C. Probably it begins to melt at 50°, and gradually passes over into the α-modification; it slowly evaporates, even at the ordinary temperature. It forms fine, feathery, asbestos-like, white needles. The β-anhydride is probably a polymer of the α-modification. Buff (*Ann. Chem. Pharm., Suppl.*, iv. p. 151) confirms this. According to R. Weber, however (Poggendorff's *Ann.*, clix. p. 313; *Berl. Ber.*, xix. p. 3187), the sulphur trioxide, obtained absolutely pure and free from water by his method, is at the summer temperature a very mobile, colourless liquid, which, on gradually cooling, solidifies to long, transparent, prismatic crystals, similar to nitrate of potash, quite different from the white, opaque crystals of the ordinary anhydride containing a little water. These crystals melt at 14°·8 C., and boil at 46°·2. Under certain conditions the anhydride can, like many other bodies, be cooled much below its proper melting-point without solidifying, but then solidifies suddenly. After a twelvemonth it still shows the same composition and the same melting-point as it had when freshly prepared. Weber accordingly rejected the assumption of two different modifications, and ascribed the phenomena of this kind observed by others, especially the formation of the modification resembling asbestos, to a minute residue of water. So much seems to be correct in Weber's conclusions that the transition of the first to the second modification is promoted by a minute quantity of water.

Oddo, in 1901 (*Rend. Acc. Lincei* [5], x. p. 207; *Chem. Centr.*, 1901, ii. p. 969), definitely proved the existence of two modifications by cryoscopic estimation of the molecular weights. The compound melting at 13°·8 is the real sulphur trioxide, SO_3; the fibrous compound, which does not melt unchanged, but at 50° slowly, and at 100° quickly changes into SO_3, is disulphuric anhydride, S_2O_6. SO_3 instantly burns organic tissues and causes deep wounds; S_2O_6 is much less active and can be touched with the hand. SO_3 dissolves at once in H_2SO_4; S_2O_6 but slowly. Oddo gives the structural formula of



Schenck (*Lieb. Ann.*, cccxvi. p. 1) regards the liquid modification as a solution of the asbestos-like polymer in real SO_3 in a state of unstable equilibrium.

The heat of formation of 1 mol. of SO_3 (=80·06 parts by weight) from S and O_3 is = 103,230 cals. (Thomsen); from SO_2+O = 34,400 cals. in the solid state, or = 22,600 cals. in the gaseous state (Berthelot). The heat of vaporising 1 mol. SO_3 is = 11,800 cals.; that produced by dissolving 1 mol. SO_3 in a large quantity of water = 39,170 cals. (Thomsen).

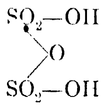
In moist air sulphuric anhydride at once forms dense white fumes; with water it hisses like red-hot iron. Many organic substances are at once charred by it. In the complete absence of water it does not redden litmus. It gives several compounds with sulphur, whose colour, with the quantity of sulphur decreasing, changes from brown to green and blue. In the blue modification Weber has proved the presence of the sesquioxide, S_2O_3. With sulphur dioxide it seems to form a distinct compound, SO_2+2SO_3. With water SO_3 at once combines to form sulphuric acid (SO_4H_2) and its different hydrates. It is, however, not easy to completely condense the sulphuric anhydride often produced in considerable quantity in technical processes, even with a large quantity of water and manifold contact, and special precautions have to be taken for this purpose.

The anhydride SO_3, when conducted through a red-hot tube, splits up into SO_2 and O, but is re-formed from these gases at a somewhat lower temperature, especially in the presence of platinum and several metallic oxides. The technical application of this reaction is described in Chapter XI. Briner and Wroszynski (*Comptes rend.*, cxlviii. p. 1518; *Chem. Centr.*, 1909, ii. p. 255) obtained SO_3 by the reaction of NO on SO_2, with formation of elementary nitrogen.

For scientific purposes sulphuric anhydride is made by gently heating fuming oil of vitriol, or by igniting sodium pyrosulphate ($Na_2S_2O_7$). Its production in a perfectly pure state is described by Weber (*loc. cit.*). Formerly it was not used for technical purposes, owing partly to the costliness of its production, partly to the supposed difficulty of handling and keeping it. Recently, however, its production has been made so much cheaper that certain branches of manufacture already employ it advantageously. Its application has turned out to be a very simple affair, as it can be sent out in drums made of tinned iron. Its handling is certainly unpleasant, since the contact of the skin with liquid anhydride, or even just liquefying by absorbing moisture, causes very malignant and slow-curing burns. Its production on a manufacturing scale will be described in Chapter XI.

PYROSULPHURIC ACID, $S_2O_7H_2$

Structural formula:



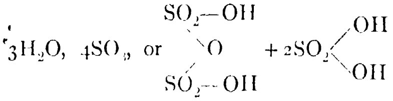
$$\begin{matrix} SO_2\text{—}OH \\ \quad\rangle O \\ SO_2\text{—}OH \end{matrix}$$

contains the elements of 80·89 parts of sulphuric anhydride and 10·11 of water, or equal molecules of hydrate and anhydride. A transparent crystalline mass, melting at 35° C., it decomposes at moderate heat into anhydride (SO_3) and oil of vitriol (SO_4H_2).

Pyrosulphuric acid is contained in the Nordhausen fuming acid of trade, which often consists altogether of it, and then bears the trade name "solid oleum." Pyrosulphuric acid can also be easily obtained from the ordinary liquid fuming Nordhausen acid by cooling below 0°. Lastly, it can be made by carefully mixing sulphur trioxide with a small quantity of oil of vitriol. Weber (*loc. cit.*) obtained an intermediate hydrate, H_2SO_4, $3SO_3$, corresponding to 94·69 per cent. of SO_3.

Pyrosulphuric acid forms salts, of which those of the alkaline metals are the best known and most important. Sodium pyrosulphate ($S_2O_7Na_2$) is formed by fusing acid sodium sulphate (SO_4NaH) at incipient red-heat. At a full red-heat it splits up further into neutral sulphate (SO_4Na_2) and sulphuric anhydride (SO_3); this reaction is sometimes utilised for producing the latter compound. In contact with water, the pyrosulphates are gradually retransformed into acid sulphates.

A compound with 14·44 per cent. H_2O can also be obtained, which crystallises in thin transparent prisms, fumes in the air, and melts at 26° C. Formula—



$$3H_2O,\ 4SO_3,\ \text{or}\ \begin{matrix} SO_2\text{—}OH \\ \diagdown \\ O \\ \diagup \\ SO_2\text{—}OH \end{matrix} + 2SO_2 \begin{matrix} \diagup OH \\ \diagdown OH \end{matrix}$$

Nordhausen or *fuming oil of vitriol*, the manufacture of which will be described in Chapter XI., is a viscous oil, representing a mixture of pyrosulphuric acid or sulphur trioxide with sulphuric hydrate in varying proportions, and therefore solidifying at very different temperatures. It fumes in the air, and gives out vapours of anhydride, whilst monohydrate remains behind. Water transforms it at once into ordinary sulphuric acid, with strong evolution of heat. It is often coloured brown by organic substances, and, according to its mode of preparation, contains many other impurities, such as iron, sodium, calcium, aluminium, etc. (as sulphates), sulphurous acid, selenium, etc. When the receivers used in its preparation are charged with ordinary strong acid, the impurities of the latter will likewise pass into the fuming acid.

The subjoined tables refer to the mixtures of SO_3 and H_2SO_3, comprised under the designation of *fuming oil of vitriol* (abridged O.V.), even when they consist mostly of SO_3 and are solid at the ordinary temperatures.

Melting-points of Fuming O.V.—Knietsch (*Ber*, 1901, p. 4100) gives the following table of the fusing-points of fuming sulphuric acid (*cf.* also under "Sulphuric Acid" below):—

Per cent. SO_3.	Melting-point C	Per cent SO_3.	Melting-point °C.
0	+10·0	55	+18·4
5	+ 3·5	60	+ 0·7
10	- 4·8	65	+ 0·8
15	-11·2	70	+ 9·0
20	-11·0	75	+17·2
25	- 0·6	80	+22·0
30	+15·2	85	+33·0 (27·0)[*]
35	+26·0	90	+34·0 (27·7)
40	+33·8	95	+36·0 (26·0)
45	+34·8	100	+40·0 (17·7)
50	+28·5		

[*] The numbers in brackets denote the fusing-points of fresh, not yet polymerised acids.

The *boiling-points* of fuming O.V. are stated by Knietsch (*loc. cit.*, p. 4110) as follows:—

SO_3 total per cent	SO_3 free per cent	Boiling-point C.	Barometric pressure, mm.
82·3	3·64	212	759
83·4	9·63	170	759
86·45	26·23	125	759
89·5	42·84	92	759
93·24	63·20	60	759
99·5	97·2	43	759

The *vapour-pressures* of various descriptions of fuming O.V. are given in the same place; *cf.* also the curves, *infrà*, p. 291.

Specific Gravities of Fuming O.V.—Cl. Winkler gives the following table of the specific gravities of fuming sulphuric acid at 20° C.; but it should be remarked that he worked only with "commercial acid," made by the old process, and that consequently all the densities found are sensibly higher than those belonging to pure acids; nor is it a matter of surprise that the values found by Messel with another description of "commercial acid" (see below) do not entirely agree with Winkler's table.

Specific gravity at 20° C.	Percentage of		Percentage of		Percentage of	
	SO_3	H_2O.	SO_3.	Acid of 66 B.	Free SO_3	H_2SO_4.
1·860	81·84	18·16	26·45	73·55	1·54	98·46
1·865	82·12	17·88	27·57	72·43	2·66	97·34
1·870	82·41	17·59	28·76	71·24	4·28	95·76
1·875	82·63	17·37	29·95	70·05	5·44	94·56
1·880	82·81	17·19	30·38	69·62	6·42	93·58
1·885	82·97	17·03	31·03	68·97	7·29	92·71
1·890	83·13	16·87	31·67	68·23	8·16	91·84
1·895	83·43	16·66	32·52	67·48	9·34	90·66
1·900	83·48	16·52	33·09	66·91	10·07	89·93
1·905	83·57	16·43	33·46	66·54	10·56	89·44
1·910	83·73	16·27	34·10	65·91	11·43	88·57
1·915	84·08	15·92	35·52	64·48	13·33	86·67
1·920	84·56	15·44	37·27	62·73	15·95	84·05
1·925	85·06	14·94	39·49	60·51	18·67	81·33
1·930	85·57	14·43	41·56	58·44	21·34	78·66
1·935	86·23	13·77	44·23	55·77	25·65	74·35
1·940	86·78	13·22	46·46	53·54	28·03	71·97
1·945	87·13	12·87	47·88	52·12	29·94	70·06
1·950	87·41	12·59	49·01	50·99	31·46	68·54
1·955	87·65	12·35	49·98	50·02	32·77	67·23
1·960	88·22	11·78	52·29	47·71	35·87	64·13
1·965	88·93	11·08	55·13	44·87	39·68	60·32
1·970	89·83	10·17	58·81	41·19	44·64	55·36

Messel (*J. Soc. Chem. Ind.*, 1885, p. 573) gives the following specific gravities of commercial Nordhausen acids, both at 26°·6 C., as determined by himself, and calculated for 15°·5 C.:—

Specimens.	Percentage of SO_3.	Specific gravities.	
		At 80° F. (=26°·6 C.)	Calculated for 60° F. (=15°·5 C.)
Liquid	8·3	1·842	1·852
"	30·9	1·930	1·940
Crystalline mass, resembling nitre.	40·0	1·956	1·970
" " .	44·5	1·961	1·975
" " .	46·2	1·963	1·977
" " .	59·4	1·980	1·994
Liquid	60·8	1·992	2·006
"	65·0	1·992	2·006
"	69·4	2·002	2·016
Crystallised	72·8	1·984	1·988
"	80·0	1·959	1·973
"	82·0	1·953	1·967

Knietsch (*Ber.*, 1901, p. 4101) gives the following tables for commercial fuming O.V., made by the contact process:—

Specific Gravities at 15° and 45° C.

H_2SO_4 per cent.	Total SO_3 per cent.	Free SO_3 per cent.	Specific gravity at 15° C	Specific gravity at 45° C.
95·98	78·35		1·8418	
96·68	78·92		1·8429	
96·99	79·18	...	1·8431	
97·66	79·72	.	1·8434 max.	
98·65	80·53	..	1·8403	
99·40	81·14	..	1·8388 min.	
99·76	81·44		1·8418	
100·00	81·63	0·0	1·8500	1·822
	83·46	10·0	1·888	1·858
	85·30	20·0	1·920	1·887
	87·14	30·0	1·957	1·920
	88·97	40·0	1·979	1·945
	90·81	50·0	2·009	1·964 max.
	92·65	60·0	2·020 max.	1·959
	94·48	70·0	2·018	1·942
	96·32	80·0	2·008	1·890
	98·16	90·0	1·990	1·864
	100·00	100·0	1·984	1·814

Specific Gravities of Fuming O.V. at 35° C.

Total SO_3 per cent.	Free SO_3 per cent.	Specific gravity.	Total SO_3 per cent.	Free SO_3 per cent.	Specific gravity.
81·63	0	1·8186	91·18	52	1·9749
81·99	2	1·8270	91·55	54	1·9760
82·36	4	1·8360	91·91	56	1·9772
82·73	6	1·8425	92·28	58	1·9754
83·09	8	1·8498	92·65	60	1·9738
83·46	10	1·8565	93·02	62	1·9709
83·82	12	1·8627	93·38	64	1·9672
84·20	14	1·8692	93·75	66	1·9636
84·56	16	1·8756	94·11	68	1·9600
84·92	18	1·8830	94·48	70	1·9564
85·30	20	1·8919	94·85	72	1·9502
85·66	22	1·9020	95·21	74	1·9442
86·03	24	1·9092	95·58	76	1·9379
86·40	26	1·9158	95·95	78	1·9315
86·76	28	1·9220	96·32	80	1·9251
87·14	30	1·9280	96·69	82	1·9183
87·50	32	1·9338	97·05	84	1·9115
87·87	34	1·9405	97·45	86	1·9046
88·24	36	1·9474	97·78	88	1·8980
88·60	38	1·9534	98·16	90	1·8888
88·97	40	1·9584	98·53	92	1·8800
89·33	42	1·9611	98·90	94	1·8712
89·70	44	1·9643	99·26	96	1·8605
90·07	46	1·9672	99·63	98	1·8488
90·44	48	1·9702	100·00	100	1·8370
90·81	50	1·9733			

The weighings were made at 15°, referred to water of 15°, with brass weights without reduction to a vacuum.[1] The temperatures to which they refer are 35° and 45°, for fuming O.V., and 15° for this and the strongest ordinary acids.

The curves (p. 290) show a maximum for ordinary acid slightly *below* the percentage of monohydrate (H_2SO_4); for fuming acids the maximum is at 60 per cent. free SO_3 at 15° C., at 56 per cent. SO_3 at 35° C., at 50 per cent. SO_3 at 45° C.

The *specific heats* were found by Knietsch as follows (those marked * were directly observed):—

Total SO_3 per cent.	Free SO_3 per cent.	Specific heat.	Total SO_3 per cent.	Free SO_3 per cent.	Specific heat.
76·8	.	0·3691*	91	51·0	0·370
78·4	...	0·3574*	92	56·45	0·400
80	.	0·350	93	61·89	0·425
80·0	.	0·3574*	93·3	63·5	0·4325*
81·5	.	0·3478*	94	67·34	0·455
82	2·0	0·345	94·64	70·6	0·4730*
83·46	10·0	0·3417*	95	72·78	0·495
84	12·89	0·340	96	78·23	0·535
85·48	20·95	0·3391*	96·52	81·0	0·5598*
86	23·78	0·340	97	83·67	0·590
87·13	29·74	0·3392*	97·92	88·6	0·6526*
88	34·67	0·350	99	89·12	0·650
88·75	38·75	0·3498*	99	94·56	0·710
90	45·56	0·360	99·8	98·9	0·7413*
90·1	46·1	0·3599*	100	100·0	0·770
90·73	49·4	0·3660*			

The *heats of solution* were observed by Knietsch both by means of a calorimeter and on a large scale. Those referring to fuming O.V. are given here, those of ordinary sulphuric acid under that heading.

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[1] The values for acids of 100 per cent. H_2SO_4 and below do not quite agree with those found by Lunge and Naef (*cf.* later on), which could not be otherwise, as the latter worked with *pure* acids and referred their figures to water of 4° C. and to the vacuum. The only essential deviation is that Knietsch does not, like the authors mentioned, as well as Kohlrausch and Schertel, find the minimum specific gravity at 100 per cent. H_2SO_4, but at 99·40 per cent.

SO_3 total per cent	SO_3 free per cent.	Calories.	Heat of solution of *solid* O.V.
82	2·0	199	
83	7·5	210	
84	12·9	223·5	...
85	18·3	237·5	
86	23·5	250	...
87	29·2	265	.
88	34·7	278	.
89	40·1	292	..
90	45·6	308	286
91	51·0	325	304
92	56·4	344	322
93	61·9	363	340
94	67·3	381	360
95	72·8	401	380
96	78·3	421	402
97	83·7	442	423
98	89·1	465	442
99	94·6	490	463
100	100·0	515	486

Knietsch (*loc. cit.*) gives also tables of the *electrical resistance*, the *velocity of outflow* (viscosity), and the *capillary rising* of sulphuric acids and O.V. from 0 per cent. to 100 per cent. SO_3; the results are exhibited in the curves, *infrà*, p. 291.

The action of fuming O.V. on *iron* (cast iron, wrought iron, and steel) will be mentioned later on, together with that of ordinary acids.

The *analysis* of fuming sulphuric acid is described after that of ordinary acid.

SULPHURIC ACID, H_2SO_4.

Natural occurrence.—Free sulphuric acid is found very exceptionally in nature, whilst some sulphates, especially that of calcium, occur in enormous quantities.

In the free state sulphuric acid has been found especially in a few springs of volcanic origin, and in the rivers fed by those springs. One of the best known cases of this kind is the Rio Vinagre in Mexico, which contains 0·111 per cent. free sulphuric acid (calculated as SO_3), and 0·091 per cent. free HCl; it daily carries into the sea 38 tons, according to others even 69 tons of both acids. Many other similar instances have been discovered in various parts of the world (*cf.* the first edition of this work, I. p. 17). Other cases again occur from the oxidation of sulphur ores, the acids being expelled by heat from the sulphates generated at first.

Miners are only too familiar with the occurrence of free acid in pit-waters from similar causes, by the corrosion of metal pumps and steam-boilers; even the leather of the valves thereby becomes brittle and the wooden parts are charred. In the case of volcanoes, sulphuric acid is formed by the oxidation of the sulphuretted hydrogen and the sulphur dioxide from the fumaroles and solfataras.

Even in the animal kingdom free sulphuric acid has been found, viz. in the salivary glands of several mollusks, especially of *Dolium galea*, which contain 2·47 per cent. free sulphuric acid and 0·4 per cent. free hydrochloric acid (Boedeker and Troschel; De Luca and Panceri).

Properties of Pure "Monohydrated" Sulphuric Acid, H_2SO_4.

The proper sulphuric hydrate, commonly known as monohydrated sulphuric acid, has the rational formula,

$$SO_2\begin{matrix}-OH\\-OH\end{matrix}$$

and may be considered as containing 81·63 per cent. SO_3 and 18·37 per cent. water. It is a limpid, colourless, oily liquid. Its sp. gr. at 0° is 1·853; at 15° (compared with water of 4°): 1·8384 (Lunge and Naef), 1·8378 (Schertel), 1·8372 (Marignac, F. Kohlrausch, Mendelejeff).[1] The specific gravity changes to the extent of ±0·001 for each degree Centigrade. Both the addition of very little SO_3 and that of very little water raises the specific gravity (see below). The pure monohydrate solidifies at about 0° and forms large, plate-shaped crystals which melt at +10°·5; they remain liquid a good deal below that temperature, but solidify on agitation, or even better when a fragment of the solid hydrate is introduced. The acid begins to boil at 290°, but the boiling-point rises up to 338° (Marignac). This shows that it does not distil unchanged; in fact a mixture of hydrated acid, anhydride, and water passes over (see below). This dissociation begins much earlier; the pure monohydrate produces fumes by giving off SO_3, very slightly even at the ordinary summer temperature, distinctly at 30° or 40°. Accordingly it cannot be obtained by boiling down or distilling dilute acid, but by adding an exactly sufficient quantity of anhydride to the strongest acid obtainable by concentration, or by cooling such acid below 0° and several times recrystallising the monohydrate in the same way. The latter process has been made commercially available by myself for the manufacture of monohydratic sulphuric acid, which consequently is no longer a laboratory product, but has become an important article of commerce (*cf.* Chapter IX.).

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[1] Cf. *Berl. Ber*., 1884, pp. 1748, 2536, 2711.

The *vapour* of sulphuric acid consists for the most part, or even entirely (according to the temperature), not of molecules of SO_4H_2, but of isolated molecules of SO_3 and H_2O; theory would give to SO_4H_2 (2 vols.) a vapour-density of 3·862, for separated molecules of SO_3 and H_2O (4 vols.) a vapour-density of 1·6931, whilst Deville and Troost at 440° found it actually = 1·74. The dissociation is therefore as good as complete in the state of vapour; and this assumption agrees very well with our present notions concerning the state of vapour (Dittmar, *Chem. News*, xx. p. 258).

Oddo and Anelli (*Gazz. Chim. Ital.*, 1911, p 552; *Chem. Zeit.*, 1911, p. 846) found the vapour-density of absolutely pure H_2SO_4 rather higher than calculated for this formula, which proves that some molecules of $(H_2SO_4)_2$ are present, as well as H_2SO_4, SO_3, and H_2O. In *solutions* they assume the sulphuric acid to be always present as the dimeric molecule $(H_2SO_4)_2$, but nitric acid as the simple molecule HNO_3.

Further detailed investigations on the properties of absolutely pure H_2SO_4 have been made by Lichty (*J. Amer. Chem. Soc.*, 1908, xxx. pp. 1834-1846), and by Hantzsch (*Z. physik. Chem.*, 1907, lxi. pp. 257-312; *Chem. Zeit.*, 1908, i. pp. 1240-1242).

Formation of Sulphuric Acid.—It has been asserted that sulphuric acid is formed in damp flowers of sulphur, even at the ordinary temperature; this is certainly the case on heating sulphur with water at 200° C., or by applying the electric current. Sulphur is easily oxidised to sulphuric acid by chlorine, hypochlorous acid, nitric acid, aqua regia, etc. It is produced, together with sulphurous acid and sulphur, from tri-, tetra-, and pentathionic acids — from the former by merely heating, from all three by the action of chlorine or bromine, or even on the prolonged action of stronger acids, which set the thionic acids free; also the thiosulphates yield sulphuric acid under the action of chlorine. All these decompositions have to be kept in view in manufacturing-processes.

Mostly sulphuric acid is produced from sulphur dioxide. The aqueous solution of the latter is gradually transformed into sulphuric acid by the action of the air alone, and it is so transformed at once by chlorine, bromine, iodine, hypochlorous acid, nitric acid, and several metallic salts, such as manganic sulphate, mercurous nitrate, etc. Sulphur dioxide and oxygen conducted through a red-hot tube containing platinum, platinised asbestos, ferric oxide, and a number of other substances, yield sulphuric anhydride, or in the presence of water sulphuric acid. This reaction, which was formerly only of scientific interest, has become of the greatest technical importance and is, according to some opinions, destined to supersede the formerly universal, and, up to this, most general process of making sulphuric acid from sulphur dioxide, air, and water by means of nitrogen oxides as oxygen carriers. All this will be explained in detail later on.

The action of *light* on the formation of SO_3 from SO_2 and O has been studied by Coehn and Becker (*Z. physik. Chem.*, 1909, lxx. pp. 88-115).

The heat of formation of 98 parts SO_4H_2 is :—

	Liquid.	In diluted solutions.
From SO_2, O, H_2O .	54,400	72,000 calories
„ S, O_3, H_2O .	124,000	141,000 „
„ S, O_4, H_2 .	193,000	210,000 „

The heat of neutralisation of 1 mol. (98 parts) H_2SO_4 by 2 mols. (80 parts) NaOH in the presence of 400 mols. of water is given by Thomsen = 31,380 cals. Pickering (*J. Chem. Soc.*, 1889, p. 323) states it only = 28,197 cals.

Sulphuric Acid containing Water.

Hydrates of Sulphuric Acid.—All observers agree that the solutions of sulphuric acid contain different *hydrates.* The literature of this subject is very large, and we shall here quote only the most important facts (*cf.* also Mendelejeff, *suprà*, p. 286, and Pickering, p. 289). A sesquihydrate of sulphuric acid cannot be established as a certain chemical compound, but the *double hydrate*, $SO_4H_2+H_2O$, is known with certainty. It crystallises from rather more dilute acid—for instance, acid of 144° Tw. in the cold. It contains 84·48 monohydrate +15·52 water (or 68·97 anhydride +31·03 water), melts at +8° C., but, owing to superfusion, generally only solidifies below this temperature (for instance, in the depth of winter); at 205° to 210° C. it already loses 1 mol. H_2O and leaves ordinary oil of vitriol behind. The crystals form large, clear, hexagonal columns with six-pointed end-faces. Sp. gr. 1·78 to 1·79. By the crystallisation of this hydrate carboys are often cracked in winter; acid of 144° Tw. and the like ought therefore only to be warehoused in places where the temperature will not sink too low, for instance below the acid-chambers. Stronger or weaker acid can be exposed to the cold of winter without any danger.

A third hydrate, $SO_4H_2+2H_2O$, is assumed, because, on diluting strong vitriol with water down to this point (that is, corresponding to 73·13 per cent. monohydrate, or 59·70 per cent. anhydride), the largest contraction, viz., from 100 vols. to 92·14 vols., takes place. Bourgoin (*Bull. Soc. Chim.* [2], xii. p. 433) infers the same from observations on electrolysing dilute vitriol. The density of this mixture is variously stated by different observers:—by Graham at 1·6321; by Bineau, 1·665; by Kolb, 1·652; by Jacquelain, 1·6746. According to Liebig it boils at 163° to 170°; between 193° and 199° it loses 1 mol. of water, and is changed into $SO_2H_2+H_2O$ (Graham).

Pickering (*Chem. News*, lx. p. 68) has obtained a hydrate of the formula H_2SO_4, $4H_2O$, containing 57·66 per cent. real sulphuric acid. It fuses at −25°. By adding a little water or sulphuric acid the fusing-point is at once lowered to −70°.

Ordinary Concentrated Oil of Vitriol.—The strongest oil of vitriol obtainable by boiling-down ordinary pure sulphuric acid contains a quantity of water which is not stated alike by different observers (Marignac, Pfaundler, Roscoe, Dittmar, Lunge and Naef, etc.). The statements differ from 97·86 to 98·99 per cent. of SO_4H_2; it is at all events very nearly 98·3 per cent. This *distilled sulphuric acid* solidifies a little below 0°; but it also shows the phenomenon of superfusion in a very high degree. It boils at 338° (Marignac), or 315° to 317° C. (Pfaundler and Pölt). Usually Marignac's statement is considered as correct; the acid of Pfaundler and Pölt probably contained a little more water. The boiling takes place quietly under a stronger pressure than the ordinary one, but at a lower pressure with violent bumping, which can be avoided by putting in platinum wire or scraps, according to Dittmar even better by conducting a slow current of air through it during the boiling (see Chapter VIII., Purification of Sulphuric Acid).

This acid of 98·3 per cent. H_2SO_4, distilling unchanged, possesses a number of other peculiarities, marking it out as representing a certain equilibrium, or so-called "critical concentration." This comes out very well in a series of curves, illustrating the properties of sulphuric acid of various degrees of concentration, as given by Knietsch (*Ber.*, 1901, p. 4089), Fig. 51, p. 291. The course of boiling-points at that concentration (330°) shows a sharp apex; below this, water or dilute sulphuric acid, above this, sulphuric anhydride is volatilised until in either case the constantly-boiling acid of 98·3 per cent. is reached. The vapour-tension at that critical concentration is = zero, measured at 100° in a vacuum; the specific gravity of hydrated acid here reaches its maximum, from which it descends in both directions; the electrical resistance at this point begins to increase suddenly towards a maximum reached at nearly 100 per cent. H_2SO_4; in connection with this the action upon iron decreases, which is of great importance for the durability of apparatus (*cf.* below).

In Fig. 51, curve 1, marked ——, shows the melting-points; curve 2, — · — · — · the specific gravities at 15°, — · · — · · at 35°; curve 3, – – – –, the specific heats; curve 4, · · · · ·, the heat of solution; curve 5, o—o—o, the electric resistance at 25°; curve 6, + — + —, the boiling-points; curve 7, · + · — · + · —, the vapour-tensions at 100°; curve 8, – – · o · — · o · —, the viscosities (times of outflow); curve 9, –·–·–·–, the capillarity; curve 10, ·|·|·|·|·|·|·, the action upon iron.

The following fact concerning a property of sulphuric acid containing about 98 per cent. H_2SO_4 is of great importance in the manufacture of sulphuric acid from SO_3 by the contact process. Knietsch found that the task of converting the SO_3 into hydrated acid cannot be accomplished by absorbing it in a series of vessels filled with water or dilute acid, although the heat of dissolution in this case is at a maximum; but acid of

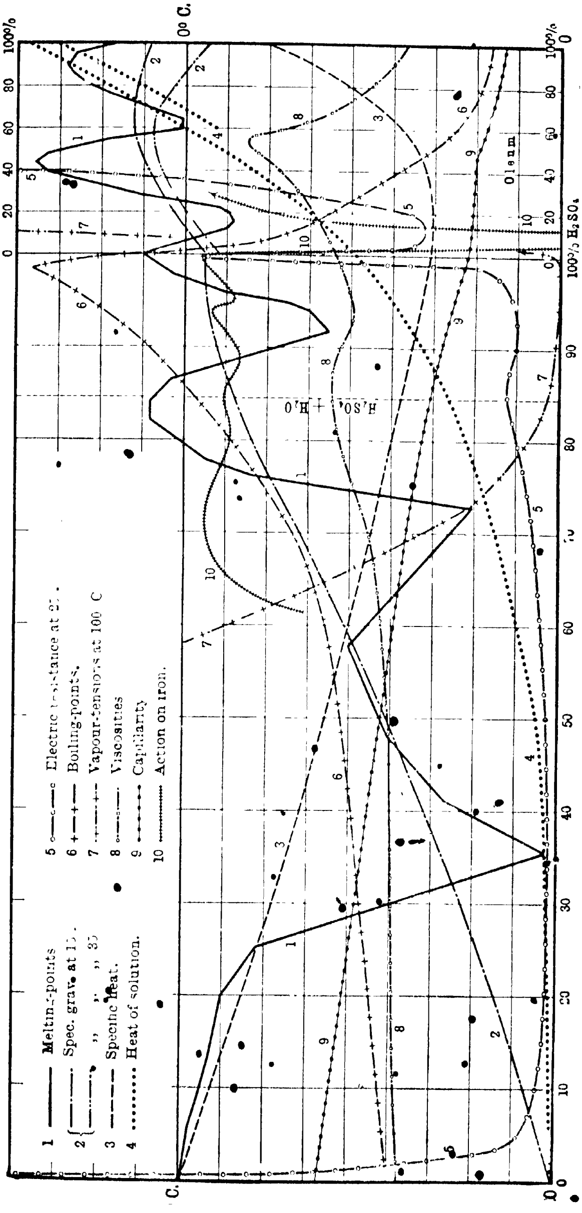
100%
80
60
40
20
0
0° C.
C.
D.
100%
0
Oleum
100% H_2SO_4
$H_2SO_4 + H_2O$
90
80
70
60
50
40
30
20
10
0
1 Melting-points
2 Spec. grav. at 15°.
,, ,, ,, 35
3 Specific heat.
4 Heat of solution.
5 Electric resistance at 2?.
6 Boiling-points.
7 Vapour-tensions at 100 C
8 Viscosities
9 Capillarity
10 Action on iron.

FIG. 51.

is slightly dissociated into H_2SO_4, H_2O+SO_3 (*cf.* p. 287), *but in the presence of very little water (equal to 98 per cent.* H_2SO_4) the partial pressure of SO_3 is at a minimum, and hence this acid has the maximum absorbing power for SO_3. Up to this point *no free* H_2O is present, but with greater dilution it is found. That these dilute acids are inferior solvents of SO_3 is explained by the fact observed by Oddo (*cf.* p. 278) that the true SO_3, melting at 14°, is easily dissolved in H_2SO_4, but the polymer, S_2O_6, but slowly. Now the latter is formed from SO_3 by the influence of minute quantities of water, and therefore also when SO_3 is passed into acids below 98 per cent. H_2SO_4.

The ordinary "*rectified oil of vitriol*" always contains more water than the acid obtainable by the highest degree of concentration or distillation. Exceptionally 98 per cent. acid is made for commercial purposes; the usual rectified O.V., formerly called 170° Tw., now more accurately 168° Tw., varies in strength from 96 down to 93 or even 92 per cent. of real monohydrate. This variation is partly caused by the fact that at the higher degrees of concentration a slight difference in specific gravity corresponds to a great difference in percentage; partly by the fact that the specific gravity of commercial acids, owing to the presence of impurities, is always higher than that of the pure acid; but, apart from this, the correctness of ordinary *hydrometers* is rarely of a very high order. Still, it must be conceded that in England at least there is a possibility of making the hydrometers all alike, the basis of Twaddell's system being plain and unmistakable, since every degree is equal to a difference of 0·005. But matters are far worse on the Continent and in America, where Baumé's hydrometer is almost universally used; unfortunately the degrees of this instrument, as stated by various authorities, answer to very different specific gravities, and those of the instruments found in trade often show even far greater deviations. The only rational hydrometer on Baumé's system which rests on a mathematical basis, and which [illegible] therefore be always obtainable with a uniform scale, is it graduated according to the formula

$$d = \frac{144{\cdot}3}{144{\cdot}3 - n},$$

where d signifies any special density (specific gravity), and n the degree of the scale corresponding to it. (The mathematical

Comparison of Baumé's Hydrometers with the Specific Gravities.

Degrees.	Rational Hydrometer, $d = \frac{144{\cdot}3}{144{\cdot}3 - n}$.	Baumé's Hydrometer (Gerlach).	American Hydrometer.	Degrees	Rational Hydrometer, $d = \frac{144{\cdot}3}{144{\cdot}3 - n}$.	Baumé's Hydrometer (Gerlach).	American Hydrometer
1	1·007	1·0068	1·005	36	1·332	1·3250	1·334
2	1·014	1·0138	1·011	37	1·345	1·3370	1·342
3	1·022	1·0208	1·023	38	1·357	1·3494	1·359
4	1·029	1·0280	1·029	39	1·370	1·3619	1·368
5	1·037	1·0353	1·036	40	1·383	1·3746	1·386
6	1·045	1·0426	1·043	41	1·397	1·3876	1·395
7	1·052	1·0501	1·050	42	1·410	1·4009	1·413
8	1·060	1·0576	1·057	43	1·424	1·4143	1·422
9	1·067	1·0653	1·064	44	1·438	1·4281	1·441
10	1·075	1·0731	1·071	45	1·453	1·4421	1·451
11	1·083	1·0810	1·086	46	1·468	1·4564	1·470
12	1·091	1·0890	1·093	47	1·483	1·4710	1·480
13	1·100	1·0972	1·100	48	1·498	1·4860	1·500
14	1·108	1·1054	1·107	49	1·514	1·5012	1·510
15	1·116	1·1138	1·114	50	1·530	1·5167	1·531
16	1·125	1·1224	1·122	51	1·540	1·5325	1·541
17	1·134	1·1310	1·136	52	1·563	1·5487	1·561
18	1·142	1·1398	1·143	53	1·580	1·5652	1·573
19	1·152	1·1487	1·150	54	1·597	1·5820	1·594
20	1·162	1·1578	1·158	55	1·615	1·5993	1·616
21	1·171	1·1670	1·172	56	1·634	1·6169	1·627
22	1·180	1·1763	1·179	57	1·652	1·6349	1·650
23	1·190	1·1858	1·186	58	1·671	1·6533	1·661
24	1·200	1·1955	1·201	59	1·691	1·6721	1·683
25	1·210	1·2053	1·208	60	1·711	1·6914	1·705
26	1·220	1·2153	1·216	61	1·732	1·7111	1·727
27	1·231	1·2254	1·231	62	1·753	1·7313	1·747
28	1·241	1·2357	1·238	63	1·774	1·7520	1·767
29	1·252	1·2462	1·254	64	1·796	1·7731	1·793
30	1·263	1·2569	1·262	65	1·819	1·7948	1·814
31	1·274	1·2677	1·269	66	1·842	1·8171	1·835
32	1·285	1·2788	1·285				
33	1·297	1·2901	1·293				
34	1·308	1·3015	1·309				
35	1·320	1·3131	1·317				

Comparison between the Degrees of Twaddell's Hydrometer and Specific Gravities.

Degrees, Tw.	Specific gravity.	Degrees, Tw.	Specific gravity.	Degrees, Tw.	Specific gravity.	Degrees, Tw.	Specific gravity.
1	1·005	44	1·220	87	1·435	130	1·650
2	1·010	45	1·225	88	1·440	131	1·655
3	1·015	46	1·230	89	1·445	132	1·660
4	1·020	47	1·235	90	1·450	133	1·665
5	1·025	48	1·240	91	1·455	134	1·670
6	1·030	49	1·245	92	1·460	135	1·675
7	1·035	50	1·250	93	1·465	136	1·680
8	1·040	51	1·255	94	1·470	137	1·685
9	1·045	52	1·260	95	1·475	138	1·690
10	1·050	53	1·265	96	1·480	139	1·695
11	1·055	54	1·270	97	1·485	140	1·700
12	1·060	55	1·275	98	1·490	141	1·705
13	1·065	56	1·280	99	1·495	142	1·710
14	1·070	57	1·285	100	1·500	143	1·715
15	1·075	58	1·290	101	1·505	144	1·720
16	1·080	59	1·295	102	1·510	145	1·725
17	1·085	60	1·300	103	1·515	146	1·730
18	1·090	61	1·305	104	1·520	147	1·735
19	1·095	62	1·310	105	1·525	148	1·740
20	1·100	63	1·315	106	1·530	149	1·745
21	1·105	64	1·320	107	1·535	150	1·750
22	1·110	65	1·325	108	1·540	151	1·755
23	1·115	66	1·330	109	1·545	152	1·760
24	1·120	67	1·335	110	1·550	153	1·765
25	1·125	68	1·340	111	1·555	154	1·770
26	1·130	69	1·345	112	1·560	155	1·775
27	1·135	70	1·350	113	1·565	156	1·780
28	1·140	71	1·355	114	1·570	157	1·785
29	1·145	72	1·360	115	1·575	158	1·790
30	1·150	73	1·365	116	1·580	159	1·795
31	1·155	74	1·370	117	1·585	160	1·800
32	1·160	75	1·375	118	1·590	161	1·805
33	1·165	76	1·380	119	1·595	162	1·810
34	1·170	77	1·385	120	1·600	163	1·815
35	1·175	78	1·390	121	1·605	164	1·820
36	1·180	79	1·395	122	1·610	165	1·825
37	1·185	80	1·400	123	1·615	166	1·830
38	1·190	81	1·405	124	1·620	167	1·835
39	1·195	82	1·410	125	1·625	168	1·840
40	1·200	83	1·415	126	1·630	169	1·845
41	1·205	84	1·420	127	1·635	170	1·850
42	1·210	85	1·425	128	1·640		
43	1·215	86	1·430	129	1·645		

deduction of this formula is given in the first edition of this work, pp. 20 and 21.) This scale is now also generally accepted in Germany and France. It is the only one in which the degree 66, which is that everywhere accepted for rectified O.V., comes near the real specific gravity of pure sulphuric acid of 96 per cent., or commercial acid of 94 to 95 per cent., namely 1·840. Unfortunately, apart from various other scales, Gerlach's scale is also sometimes used, although this is far lower than the "rational" scale, and, to make the confusion still greater, the American manufacturers have adopted again another scale, based on the formula

$$n = 145 - \frac{145}{d}.$$

In order to clear the way as far as possible, we give herewith tables (pp. 293, 294) showing the value of a degree Baumé, according to the rational scale, to Gerlach's, and to the American scale (the last is copied from A. H. Elliott, *Chem. Trade J.*, ii. p. 183).

The percentage of *mixtures of sulphuric acid and water* is in the great majority of cases tested by the hydrometer only, and many tables have been constructed for this purpose. It would be very desirable, as Hasenclever points out (*Hofmann's Report*, i. p. 181), if all sulphuric-acid makers used the same reduction-tables for their calculations; for in the statements on the yield of acid, and in many other cases, frequently different tables are used; so that the working results of different factories are not always comparable with each other. This very clearly appears from the following comparative table:—

Degrees (Baumé).	Spec. grav. (Kolb)	Percentage of SO_4H_2 in the vitriol according to							
		Vauquelin.	D'Arcet.	Tables used at different factories.				Bineau.	Kolb.
10	1·075	11·73	.	11·5	11·40		10·98	11·0	10·8
20	1·162	24·01		23·3	23·46		21·97	22·4	22·2
30	1·263	36·52	...	36·9	36·60	.	35·93	34·9	34·7
40	1·383	50·41	...	51·6	51·49		49·94	38·4	48·3
50	1·530	66·54	66·45	66·9	66·17	63·8	63·92	62·7	62·5
60	1·711	84·22	82·34	83·3	82·80	79·4	79·90	78·0	78·1
66	1·842	100·00	100·00	100·0	100·00	94·0	97·87	100·0	100·0

The totally incorrect tables of Vauquelin and D'Arcet are used hardly anywhere except in the south of France.

Specific Gravities of Sulphuric Acid according to Lunge and Isler and Lunge and Naef.

Spec. grav. at $\frac{15^\circ}{4^\circ}$ (in the vacuum).	Degree, Baumé.	Degree, Twaddell	100 parts by weight of chemically pure acid contain per cent —				1 litre of chemically pure acid contains kilograms of—			
			SO_3.	H_2SO_4	Acid of 142° Tw.	Acid of 106° Tw.	SO_3	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·000	0	0	0·07	0·09	0·12	0·14	0·001	0·001	0·001	0·001
1·005	0·7	1	0·68	0·83	1·06	1·33	0·007	0·008	0·011	0·013
1·010	1·4	2	1·28	1·57	2·01	2·51	0·013	0·016	0·020	0·025
1·015	2·1	3	1·88	2·30	2·95	3·68	0·019	0·023	0·030	0·037
1·020	2·7	4	2·47	3·03	3·88	4·85	0·025	0·031	0·040	0·050
1·025	3·4	5	3·07	3·76	4·82	6·02	0·032	0·039	0·049	0·062
1·030	4·1	6	3·67	4·49	5·78	7·18	0·038	0·046	0·059	0·074
1·035	4·7	7	4·27	5·23	6·73	8·37	0·044	0·054	0·070	0·087
1·040	5·4	8	4·87	5·96	7·64	9·54	0·051	0·062	0·079	0·099
1·045	6·0	9	5·45	6·67	8·55	10·67	0·057	0·071	0·089	0·112
1·050	6·7	10	6·02	7·37	9·44	11·79	0·063	0·077	0·099	0·124
1·055	7·4	11	6·59	8·07	10·34	12·91	0·070	0·085	0·109	0·136
1·060	8·0	12	7·16	8·77	11·24	14·03	0·076	0·093	0·119	0·149
1·065	8·7	13	7·73	9·47	12·14	15·15	0·082	0·102	0·129	0·161
1·070	9·4	14	8·32	10·19	13·05	16·30	0·089	0·109	0·140	0·174
1·075	10·0	15	8·90	10·90	13·96	17·44	0·096	0·117	0·150	0·188
1·080	10·6	16	9·47	11·60	14·87	18·56	0·103	0·125	0·161	0·201
1·085	11·2	17	10·04	12·30	15·76	19·68	0·109	0·133	0·171	0·213
1·090	11·9	18	10·60	12·99	16·65	20·78	0·116	0·142	0·181	0·227
1·095	12·4	19	11·16	13·67	17·52	21·87	0·122	0·150	0·192	0·240
1·100	13·0	20	11·71	14·35	18·39	22·96	0·129	0·158	0·202	0·253
1·105	13·6	21	12·27	15·03	19·26	24·05	0·136	0·166	0·212	0·265
1·110	14·2	22	12·82	15·71	20·13	25·14	0·143	0·175	0·223	0·279
1·115	14·9	23	13·36	16·36	20·96	26·18	0·149	0·183	0·234	0·292
1·120	15·4	24	13·89	7·01	21·80	27·22	0·156	0·191	0·245	0·305
1·125	16·0	25	14·42	17·66	22·63	28·26	0·162	0·199	0·255	0·318
1·130	16·5	26	14·95	18·31	23·47	29·30	0·169	0·207	0·265	0·331

1·135	17·1	27	15·48	18·96	24·29	30·34	0·176	0·215	0·276	0·344
1·140	17·7	28	16·01	19·61	25·13	31·38	0·183	0·223	0·287	0·358
1·145	18·3	29	16·54	20·26	25·96	32·42	0·189	0·231	0·297	0·371
1·150	18·8	30	17·07	20·91	26·79	33·46	0·196	0·239	0·308	0·385
1·155	19·3	31	17·59	21·55	27·61	34·48	0·203	0·248	0·319	0·398
1·160	19·8	32	18·11	22·19	28·43	35·50	0·210	0·257	0·330	0·412
1·165	20·3	33	18·64	22·83	29·25	36·53	0·217	0·266	0·341	0·426
1·170	20·9	34	19·16	23·47	30·07	37·55	0·224	0·275	0·352	0·439
1·175	21·4	35	19·69	24·12	30·90	38·59	0·231	0·283	0·363	0·453
1·180	22·0	36	20·21	24·76	31·73	39·62	0·238	0·292	0·374	0·467
1·185	22·5	37	20·73	25·40	32·55	40·64	0·246	0·301	0·386	0·481
1·190	23·0	38	21·26	26·04	33·37	41·66	0·253	0·310	0·397	0·496
1·195	23·5	39	21·78	26·68	34·19	42·69	0·260	0·319	0·409	0·511
1·200	24·0	40	22·30	27·32	35·01	43·71	0·268	0·328	0·420	0·525
1·205	24·5	41	22·82	27·95	35·83	44·72	0·275	0·337	0·432	0·539
1·210	25·0	42	23·33	28·58	36·66	45·73	0·282	0·346	0·444	0·553
1·215	25·5	43	23·84	29·21	37·45	46·74	0·290	0·355	0·455	0·568
1·220	26·0	44	24·36	29·84	38·23	47·74	0·297	0·364	0·466	0·583
1·225	26·4	45	24·88	30·48	39·05	48·77	0·305	0·373	0·478	0·598
1·230	26·9	46	25·39	31·11	39·86	49·78	0·312	0·382	0·490	0·612
1·235	27·4	47	25·88	31·70	40·61	50·72	0·320	0·391	0·502	0·626
1·240	27·9	48	26·35	32·28	41·37	51·65	0·327	0·400	0·513	0·640
1·245	28·4	49	26·83	32·86	42·11	52·58	0·334	0·409	0·524	0·655
1·250	28·8	50	27·29	33·43	42·84	53·49	0·341	0·418	0·535	0·669
1·255	29·3	51	27·76	34·00	43·57	54·40	0·348	0·426	0·547	0·683
1·260	29·7	52	28·22	34·57	44·30	55·31	0·356	0·435	0·558	0·697
1·265	30·2	53	28·69	35·14	45·03	56·22	0·363	0·444	0·570	0·711
1·270	30·6	54	29·15	35·71	45·76	57·14	0·370	0·454	0·581	0·725
1·275	31·1	55	29·62	36·29	46·50	58·06	0·377	0·462	0·593	0·740
1·280	31·5	56	30·10	36·87	47·24	58·99	0·385	0·472	0·605	0·755
1·285	32·0	57	30·57	37·45	47·99	59·92	0·393	0·481	0·617	0·770
1·290	32·4	58	31·04	38·03	48·73	60·85	0·400	0·490	0·629	0·785
1·295	32·8	59	31·52	38·61	49·47	61·78	0·408	0·500	0·641	0·800
1·300	33·3	60	31·99	39·19	50·21	62·70	0·416	0·510	0·653	0·815
1·305	33·7	61	32·46	39·77	50·96	63·63	0·424	0·519	0·665	0·830
1·310	34·2	62	32·94	40·35	51·71	64·56	0·432	0·529	0·677	0·846

Specific Gravities of Sulphuric Acid (continued).

Spec. grav. at $\frac{15^\circ}{4}$ (in the vacuum).	Degree, Baumé.	Degree Twaddell.	100 parts by weight of chemically pure acid contain per cent.—				1 litre of chemically pure acid contains kilograms of—			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·315	34·6	63	33·41	40·93	52·45	65·45	0·439	0·538	0·689	0·860
1·320	35·0	64	33·88	41·50	53·18	66·40	0·447	0·548	0·702	0·876
1·325	35·4	65	34·35	42·08	53·92	67·33	0·455	0·557	0·714	0·892
1·330	35·8	66	34·80	42·66	54·67	68·26	0·462	0·567	0·727	0·908
1·335	36·2	67	35·27	43·20	55·36	69·12	0·471	0·577	0·739	0·923
1·340	36·6	68	35·71	43·74	56·05	69·98	0·479	0·586	0·751	0·938
1·345	37·0	69	36·14	44·28	56·74	70·85	0·486	0·596	0·763	0·953
1·350	37·4	70	36·58	44·82	57·43	71·71	0·494	0·605	0·775	0·968
1·355	37·8	71	37·02	45·35	58·11	72·56	0·502	0·614	0·787	0·983
1·360	38·2	72	37·45	45·88	58·79	73·41	0·509	0·624	0·800	0·998
1·365	38·6	73	37·89	46·41	59·48	74·26	0·517	0·633	0·812	1·014
1·370	39·0	74	38·32	46·94	60·15	75·10	0·525	0·643	0·824	1·029
1·375	39·4	75	38·75	47·47	60·83	75·95	0·533	0·653	0·836	1·044
1·380	39·8	76	39·18	48·00	61·51	76·80	0·541	0·662	0·849	1·060
1·385	40·1	77	39·62	48·53	62·19	77·65	0·549	0·672	0·861	1·075
1·390	40·5	78	40·05	49·06	62·87	78·50	0·557	0·682	0·873	1·091
1·395	40·8	79	40·48	49·59	63·55	79·34	0·564	0·692	0·886	1·107
1·400	41·2	80	40·91	50·11	64·21	80·18	0·573	0·702	0·899	1·123
1·405	41·6	81	41·33	50·63	64·88	81·01	0·581	0·711	0·912	1·138
1·410	42·0	82	41·76	51·15	65·55	81·80	0·589	0·721	0·924	1·154
1·415	42·3	83	42·17	51·66	66·21	82·66	0·597	0·730	0·937	1·170
1·420	42·7	84	42·57	52·15	66·82	83·44	0·604	0·740	0·949	1·185
1·425	43·1	85	42·96	52·63	67·44	84·21	0·612	0·750	0·961	1·200
1·430	43·4	86	43·36	53·11	68·06	84·98	0·620	0·759	0·973	1·215
1·435	43·8	87	43·75	53·59	68·68	85·74	0·628	0·769	0·986	1·230
1·440	44·1	88	44·14	54·07	69·29	86·51	0·636	0·779	0·998	1·246
1·445	44·4	89	44·53	54·55	69·90	87·28	0·643	0·789	0·010	1·261
1·450	44·8	90	44·92	55·03	70·52	88·05	0·651	0·798	0·023	1·277

1·455	45·1	91	45·31	55·50	71·12	88·80	0·659	0·808	0·035	1·292
1·460	45·4	92	45·69	55·97	71·72	89·55	0·667	0·817	0·047	1·307
1·465	45·8	93	46·07	56·43	72·31	90·29	0·675	0·828	0·059	1·323
1·470	46·1	94	46·45	56·90	72·91	91·04	0·683	0·837	0·027	1·338
1·475	46·4	95	46·83	57·37	73·51	91·79	0·691	0·846	0·084	1·354
1·480	46·8	96	47·21	57·83	74·10	92·53	0·699	0·856	1·097	1·370
1·485	47·1	97	47·57	58·28	74·68	93·25	0·707	0·865	1·109	1·385
1·490	47·4	98	47·95	58·74	75·27	93·98	0·715	0·876	1·122	1·400
1·495	47·8	99	48·34	59·22	75·88	94·75	0·723	0·885	1·134	1·417
1·500	48·1	100	48·73	59·70	76·50	95·52	0·731	0·896	1·147	1·433
1·505	48·4	101	49·12	60·18	77·12	96·29	0·739	0·906	1·160	1·449
1·510	48·7	102	49·51	60·65	77·72	97·04	0·748	0·916	1·174	1·465
1·515	49·0	103	49·89	61·12	78·32	97·79	0·756	0·926	1·187	1·481
1·520	49·4	104	50·28	61·59	78·93	98·54	0·764	0·936	1·199	1·498
1·525	49·7	105	50·66	62·06	79·52	99·30	0·773	0·946	1·213	1·514
1·530	50·0	106	51·04	62·53	80·13	100·05	0·781	0·957	1·226	1·531
1·535	50·3	107	51·43	63·00	80·73	100·80	0·789	0·967	1·239	1·547
1·540	50·6	108	51·78	63·43	81·28	101·49	0·797	0·977	1·252	1·563
1·545	50·9	109	52·12	63·85	81·81	102·16	0·805	0·987	1·264	1·579
1·550	51·2	110	52·46	64·26	82·34	102·82	0·813	0·996	1·276	1·593
1·555	51·5	111	52·79	64·67	82·87	103·47	0·821	1·006	1·289	1·609
1·560	51·8	112	53·12	65·08	83·39	104·13	0·829	1·015	1·301	1·624
1·565	52·1	113	53·46	65·49	83·92	104·78	0·837	1·025	1·313	1·640
1·570	52·4	114	53·80	65·90	84·44	105·44	0·845	1·035	1·325	1·655
1·575	52·7	115	54·13	66·30	84·95	106·08	0·853	1·044	1·338	1·671
1·580	53·0	116	54·46	66·71	85·48	106·73	0·861	1·054	1·351	1·686
1·585	53·3	117	54·80	67·13	86·03	107·41	0·869	1·064	1·364	1·702
1·590	53·6	118	55·18	67·59	86·62	108·14	0·877	1·075	1·377	1·719
1·595	53·9	119	55·55	68·05	87·20	108·88	0·886	1·085	1·391	1·737
1·600	54·1	120	55·93	68·51	87·79	109·62	0·895	1·096	1·405	1·754
1·605	54·4	121	56·30	68·97	88·38	110·35	0·904	1·107	1·419	1·772
1·610	54·7	122	56·68	69·43	88·97	111·09	0·913	1·118	1·432	1·789
1·615	55·0	123	57·05	69·89	89·56	111·82	0·921	1·128	1·446	1·806
1·620	55·2	124	57·40	70·32	90·11	112·51	0·930	1·139	1·460	1·823
1·625	55·5	125	57·75	70·74	90·65	113·18	0·938	1·150	1·473	1·840
1·630	55·8	126	58·09	71·16	91·19	113·86	0·947	1·160	1·486	1·857
1·635	56·0	127	58·43	71·57	91·71	114·51	0·955	1·170	1·499	1·873
1·640	56·3	128	58·77	71·99	92·25	115·18	0·964	1·180	1·513	1·889

Specific Gravities of Sulphuric Acid (continued).

Spec. grav. at $\frac{15^\circ}{4^\circ}$ (in the vacuum).	Degree, Baumé	Degree, Twaddell	100 parts by weight of chemically pure acid contain per cent.—				1 litre of chemically pure acid contains kilograms of—			
			SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.	SO_3.	H_2SO_4.	Acid of 142° Tw.	Acid of 106° Tw.
1·645	56·6	129	59·40	72·40	92·77	114·84	0·972	1·191	1·526	1·905
1·650	56·9	130	59·45	72·82	93·29	116·51	0·981	1·202	1·540	1·922
1·655	57·1	131	59·78	73·23	93·81	117·17	0·989	1·212	1·553	1·939
1·660	57·4	132	60·11	73·64	94·36	127·82	0·998	1·222	1·566	1·956
1·665	57·7	133	60·46	74·07	94·92	118·51	1·007	1·233	1·580	1·973
1·670	57·9	134	60·82	74·51	95·48	119·22	1·016	1·244	1·595	1·991
1·675	58·2	135	61·20	74·97	96·07	119·95	1·025	1·256	1·609	2·009
1·680	58·4	136	61·57	75·42	96·65	120·67	1·034	1·267	1·623	2·027
1·685	58·7	137	61·93	75·86	97·21	121·38	1·043	1·278	1·638	2·046
1·690	58·9	138	62·29	76·30	97·77	122·08	1·053	1·289	1·652	2·064
1·695	59·2	139	62·64	76·73	98·32	122·77	1·062	1·301	1·667	2·082
1·700	59·5	140	63·00	77·17	98·89	123·47	1·071	1·312	1·681	2·100
1·705	59·7	141	63·35	77·60	99·44	124·16	1·080	1·323	1·696	2·117
1·710	60·0	142	63·70	78·04	100·00	124·86	1·089	1·334	1·710	2·136
1·715	60·2	143	64·07	78·48	100·56	125·57	1·099	1·346	1·725	2·154
1·720	60·4	144	64·43	78·92	101·13	126·27	1·108	1·357	1·739	2·172
1·725	60·6	145	64·78	79·36	101·69	126·98	1·118	1·369	1·754	2·191
1·730	60·9	146	65·14	79·80	102·25	127·68	1·127	1·381	1·769	2·209
1·735	61·1	147	65·50	80·24	102·82	128·38	1·136	1·392	1·784	2·228
1·740	61·4	148	65·86	80·68	103·38	129·09	1·146	1·404	1·799	2·247
1·745	61·6	149	66·22	81·12	103·95	129·79	1·156	1·416	1·814	2·265
1·750	61·8	150	66·58	81·56	104·52	130·49	1·165	1·427	1·829	2·284
1·755	62·1	151	66·94	82·00	105·08	131·20	1·175	1·439	1·845	2·303
1·760	62·3	152	67·30	82·44	105·64	131·90	1·185	1·451	1·859	2·321
1·765	62·5	153	67·65	82·88	106·21	132·61	1·194	1·463	1·874	2·340
1·770	62·8	154	68·02	83·32	106·77	133·31	1·204	1·475	1·890	2·359
1·775	63·0	155	68·49	83·90	107·51	134·24	1·216	1·489	1·908	2·381
1·780	63·2	156	68·98	84·50	108·27	135·20	1·228	1·504	1·928	2·407

1·785	63·5	157	69·47	83·10	109·05	136·16	1·240	1·519	1·947	2·432
1·790	63·7	158	69·96	84·70	109·82	137·14	1·252	1·534	1·965	2·455
1·795	64·0	159	70·45	85·30	110·58	138·08	1·265	1·549	1·983	2·479
1·800	64·2	160	70·94	86·90	111·35	139·06	1·277	1·564	2·004	2·503
1·805	64·4	161	71·50	87·60	112·25	140·16	1·291	1·581	2·026	2·530
1·810	64·6	162	72·08	88·30	113·15	141·28	1·305	1·598	2·048	2·558
1·815	64·8	163	72·69	89·05	114·11	142·48	1·319	1·621	2·071	2·587
1·820	65·0	164	73·51	90·05	115·33	144·08	1·338	1·639	2·099	2·622
1·821	...		73·63	90·20	115·59	144·32	1·341	1·643	2·104	2·628
1·822	65·1	...	73·80	90·40	115·84	144·64	1·345	1·647	2·110	2·635
1·823	...	...	73·96	90·60	116·10	144·96	1·348	1·651	2·116	2·643
1·824	65·2	...	74·12	90·80	116·35	145·28	1·352	1·656	2·122	2·650
1·825	...	165	74·29	91·00	116·61	145·60	1·356	1·661	2·128	2·657
1·826	65·3	...	74·49	91·25	116·93	146·00	1·360	1·666	2·135	2·666
1·827	...	...	74·69	91·50	117·25	146·40	1·364	1·671	2·142	2·675
1·828	65·4	...	74·86	91·70	117·51	146·72	1·368	1·676	2·148	2·682
1·829	...	...	75·03	91·90	117·76	147·04	1·372	1·681	2·154	2·689
1·830	...	166	75·19	92·10	118·02	147·36	1·376	1·685	2·159	2·696
1·831	65·5	...	75·35	92·30	118·27	147·68	1·380	1·690	2·165	2·704
1·832	...	...	75·53	92·52	118·56	148·03	1·384	1·695	2·172	2·711
1·833	65·6	...	75·72	92·75	118·85	148·40	1·388	1·700	2·178	2·720
1·834		...	75·96	93·05	119·23	148·88	1·393	1·706	2·186	2·730
1·835	65·7	167	76·27	93·43	119·72	149·49	1·400	1·713	2·196	2·743
1·836	...		76·57	93·80	120·19	150·08	1·406	1·722	2·207	2·755
1·837	...	...	76·90	94·20	120·71	150·72	1·412	1·730	2·217	2·769
1·838	65·8	...	77·23	94·60	121·22	151·36	1·419	1·739	2·228	2·782
1·839	...	...	77·55	95·00	121·74	152·00	1·426	1·748	2·239	2·795
1·840	65·9	168	78·04	95·60	122·51	152·96	1·436	1·759	2·254	2·814
1·8405	...	...	78·53	95·95	122·96	153·52	1·441	1·765	2·262	2·825
1·8410	...	...	79·19	97·00	124·30	155·20	1·458	1·786	2·288	2·857
1·8415	...	...	79·76	97·70	125·20	156·32	1·469	1·799	2·305	2·879
1·8410	...	...	80·16	98·20	125·82	157·12	1·476	1·808	2·317	2·893
1·8405	...		80·57	98·70	126·48	157·92	1·483	1·816	2·328	2·906
1·8400	...	...	80·98	99·20	127·12	158·72	1·490	1·825	2·339	2·920
1·8395	...		81·18	99·45	127·44	159·12	1·494	1·830	2·344	2·927
1·8390	...	...	81·39	99·70	127·76	159·52	1·497	1·834	2·349	2·933
1·8385	...	...	81·59	99·95	128·08	159·92	1·500	1·838	2·355	2·940

We shall here not take any notice of those old tables, nor of those of Ure, Dalton, etc., and we refer to our first edition as to the more modern and reliable tables of Bineau and Kolb. In this place we give only a table (pp. 296-301) worked out from the most reliable results, viz., those of Lunge and Isler (*Z. angew. Chem.*, 1890, p. 129) for the strengths up to 142° Tw., and also of Lunge and Naef (*Chem. Ind.*, 1883, p. 37).

The specific gravities were in each case estimated by Lunge and his co-operators at exactly 15° C. and compared with water of 4°, the weighings being reduced to the vacuum. Special notice should be taken of the fact that all older tables (including those of Bineau, Otto, and Kolb) are entirely wrong in the case of the acids of highest strength, since the maximum of specific gravity does not (as it is made to do in those tables) coincide with the greatest strength, that is, pure monohydrated sulphuric acid H_2SO_4. The maximum is at about 98·5 per cent., and from this point the specific gravities decline to 100 per cent. H_2SO_4; above this point, that is when SO_3 is present, they instantly rise again. (*Cf.* Kohlrausch, *Pogg. Annal. Erganzungsband*, viii. p 675; Schertel, *J. prakt. Chem.* [2], xxvi. p. 246; Lunge and Naef, *Chem. Ind.*, 1883, p. 37; and others.)

Special attention should be drawn to the point that all tables indicate the specific gravities only for *chemically pure acids*; the figures for commercial impure acids are always higher; we shall return to this subject further on. The accuracy of the above-given tables may be taken as ±0·05, so that the first decimal is right, but the second serves only for determining the first.

A very extended study of the specific gravities of sulphuric-acid solutions has been published by Pickering (*J. Chem. Soc.*, lvii. pp. 64 *et seq.*). The reasons why I do not see any occasion for accepting Pickering's figures in lieu of my own are stated in *J. Soc. Chem. Ind.*, 1890, p. 1017. The table of A. Marshall (*ibid.*, 1902, p. 1509) is founded on Pickering's results. His method for estimating the strength of sulphuric acid solutions, *ibid.*, p. 1511, cannot vie with the ordinary titration either in speed or accuracy.

Perhaps the most elaborate investigation on the density and expansion of aqueous solutions of sulphuric acid, the formation of hydrates, etc., has been made by Domke and Bein, on behalf of the Normaleichungskommission at Berlin (*Z. anorg Chem*, 1905, xliii. pp. 125-181). Nearly all of their results sufficiently agree with those obtained by myself and my co-operators.

Worden and Motion (*J. Soc. Chem. Ind.*, 1905, pp. 178 *et seq.*) have made very accurate determinations of the density of very dilute sulphuric acid, for the purpose of preparing standard solutions for volumetric purposes. Their work has no application for technical purposes.

The table elaborated by W. C. Ferguson (*ibid.*, 1905, p. 790) deviates but slightly from that worked out by myself and my co-operators.

A paper by Mendelejeff (*Z. physik. Chem.*, i. 273) on the specific gravities of the mixtures of sulphuric acid and water has only theoretical interest.

A correction for any deviation of the temperature from 15° must be made, whenever the acid tested by the hydrometer is above or below that temperature. Bineau has given a small table for this purpose, which, however, is wrong for the more dilute acids. From a very large number of observations made in my laboratory, a table has been constructed showing the alterations to be made in the specific gravities observed for all strengths of acid, and for all temperatures from 0° to 100°, in order to reduce them to 15° C. This table is found in Lunge's *Technical Chemists' Handbook* (1910), pp. 126-129; in this place we give only the average figures. For each degree above or below 15° you should add to or deduct from the specific gravity observed:—

0·0006	with	acids up to	1·170		
0·0007	with	acids from	1·170	to	1·450
0·0008	,,	,,	1·450	,,	1·580
0·0009	,,	,,	1·580	,,	1·750
0·0010	,,	,,	1·750	,,	1·840

Influence of Impurities on the Density of Aqueous Sulphuric Acid.—The specific gravities given in all the tables refer only to *pure* acid, and cannot be accepted as quite correct for the ordinary acid of trade, which always contains impurities. Kolb has examined into this matter, and has determined the influence of the common impurities upon the density of sulphuric acid, viz., that of lead sulphate, of the oxygen compounds, of nitrogen, and of sulphurous acid. Arsenic, and perhaps iron, usually occur in too small a quantity in sulphuric acid to influence its density; but certainly there may be cases, not mentioned by Kolb, in which sulphuric acid is *strongly* contaminated with salts of iron, aluminium, sodium, etc. The iron, for instance, may come from pyrites-dust; aluminium from the packing of the Glover tower, or from the fire-clay frequently employed for stopping leaks; sodium from solutions of nitrate or sulphate of soda, which sometimes inadvertently get into the chambers.

For saturated solutions of *sulphurous acid* in sulphuric acid of varying density, Kolb (*Bull. Soc. Ind. Mulhouse*, 1872, p. 224) gave a table[1] which has been proved to be incorrect by J. T. Dunn (*Chem. News*, xliii. p. 121, and xlv. p. 270). The latter has shown that Kolb's figures are too low. By passing a current of pure dry SO_2 through sulphuric acid of sp. gr. 1·841, he found that this acid dissolves:—

Temperature.	Volume at 760 millim pressure.	Spec. grav. of solution at temp. of experiment.
°C.	Vols SO_2.	
At 11·1	33·78	1·823
" 16·1	28·86	...
" 17·1	28·14	
" 26·9	19·27	1·822
" 42·0	12·82	1·821
" 50·9	9·47	1·818
" 62·3	7·21	1·816
" 84·2	4·54	1·809

Dilute acids dissolve the following quantities, at temperatures varying from 15° to 16°, reduced to 760 mm. pressure:—

Spec grav. of sulphuric acid.	Absorbs vols. SO_2.
1·753	20·83
1·626	25·17
1·456	29·87
1·257	30·52
1·151	31·82
1·067	34·08

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[1] Given in our second edition, p. 127.

In such quantities (up to saturation) sulphurous acid certainly never occurs in commercial vitriol; and it is very rarely that more than traces of it are found therein, since it cannot co-exist with the *nitrogen oxides* which are most frequently found in commercial vitriol. *Nitric acid* is, if at all, only present in extremely small quantities in the sulphuric acid of trade, and therefore does not modify its density to a sensible extent; especially it will not be found in sulphuric acid of more than 144° Tw., except perhaps in the nitrous vitriol from the Gay-Lussac towers; but even this, according to my analyses (see below), under normal conditions contains mere traces of NO_3H. *Nitric oxide* can also be neglected; neither concentrated nor diluted sulphuric acid dissolves more than mere traces of it. *Nitrous acid* certainly has a very marked effect on the apparent percentage of a sulphuric acid, according to the hydrometrical test, although only in "nitrous vitriol" such large proportions of nitrous acid occur as to influence the specific gravity of the sulphuric acid.

Marshall (*J. Soc. Chem. Ind.*, 1902, p. 1508) shows that sulphuric acid, recovered from the *waste acid of nitrating processes*, may contain notable quantities of *nitric acid*, which make the specific gravity of strong sulphuric acid appear higher than normal. Mixtures of both acids up to 7·5 per cent. HNO_3 showed an increase of sp. gr. up to 1·862; from that onwards the specific gravities decrease. Further experiments showed that an additional 0·1 per cent. of various sulphates raises the specific gravity of strong sulphuric acid by 0·001; lead sulphate by 0·0015; As_2O_3 by 0·0013; nitrosulphuric acid by 0·00027. *Lead sulphate* is much more soluble than stated by Kolb (*suprà*, p. 304); acid of 98 per cent. may contain 0·09 per cent. $PbSO_4$, acid of 94 per cent. 0·06 per cent. $PbSO_4$.

Kolb (*loc. cit.*, and our second edition, p. 129) has given a table for the specific gravities of solutions of N_2O_3 (or rather of SO_5NH; *cf.* below) in sulphuric acid which we now omit as useless, since it is founded upon erroneous assumptions.

R. Kisling (*Chem. Ind.*, 1886, p. 137) has examined the effect of the presence of *arsenic* on the specific gravity of sulphuric acid. The specific gravities of two commercial acids, A and B, were observed at 15° C. and calculated for water of 4° C.

and the vacuum, in order to be comparable with Lunge and Naef's figures for pure acid (*suprà*, pp. 296 *et seq.*).

A.			B.		
Spec. grav. at 15°	SO_4H_2 per cent.	As_2O_3 per cent.	Spec. grav. at 15°.	SO_4H_2 per cent.	As_2O_3 per cent.
1·8377	..	0·137	1·8367	93·82	0·024
1·8387	...	0·137	1·8372	93·67	0·035
1·8393	92·87	0·192	1·8373	93·12	0·028
1·8409	93·28	0·258	1·8384	93·72	0·037
1·8412	94·25	0·219	1·8386	93·96	0·037
1·8413	93·60	0·254	1·8388	94·04	0·039
1·8414	93·93	0·231			
1·8415	93·77	0·231			...

When comparing these results with those of Lunge and Naef, the considerable influence of the arsenious acid on the specific gravity of sulphuric acid is very apparent.

With respect to *lead sulphate*, Kolb found that, at the ordinary temperature, there was dissolved up to

0·039 part in 100 parts vitriol of 1·841 sp. gr.
0·011 „ „ 100 „ „ 1·793 „ „
0·003 „ „ 100 „ „ 1·540 „ „

In more dilute acids the lead can hardly be estimated. Nitric acid, which anyhow occurs in very small quantities, does not strongly influence the solubility of lead sulphate in sulphuric acid, nitrous acid not at all. The effect of lead sulphate on the density of vitriol can accordingly be neglected for the ordinary temperature; at most it would influence the fourth place of decimals.

Although, as we see, the impurities of ordinary sulphuric acid, leaving aside "nitrous vitriol," have very little effect on its density, still the latter, at the *highest degrees of concentration*, is no trustworthy means of estimating the percentage of real SO_4H_2 in the acid, even when the correction for temperature mentioned on p. 303 is applied, because at this concentration a small difference in density corresponds to a very large difference in percentage. Many factories use special hydrometers, in which the last few degrees are spread over a large area and are further subdivided; but in fact the density ought to be estimated by more accurate methods, for the hydrometers are frequently not reliable, and certainly not so unless the normal temperature for which they have been made be *exactly* observed. But any determination of density for estimating the percentage of the very strongest acids must be rejected, after what we have seen on p. 302. The acids from 96 per cent. upwards ought therefore always to be estimated alkalimetrically.

Obtaining Acid of any Desired Strength by mixing O.V. with Water.—The following table of Anthon's will be of practical value. It shows in column *a* how many parts of oil of vitriol of 168° Tw. must be mixed with 100 parts water at 15° or 20° in order to obtain an acid of the specific gravity *b*.

a.	*b*	*a*.	*b*.	*a*.	*b*.
1	1·009	130	1·456	370	1·723
2	1·015	140	1·473	380	1·727
5	1·035	150	1·490	390	1·730
10	1·060	160	1·510	400	1·733
15	1·090	170	1·530	410	1·737
20	1·113	180	1·543	420	1·740
25	1·140	190	1·556	430	1·743
30	1·165	200	1·568	440	1·746
35	1·187	210	1·580	450	1·750
40	1·210	220	1·593	460	1·754
45	1·229	230	1·606	470	1·757
50	1·248	240	1·620	480	1·760
55	1·265	250	1·630	490	1·763
60	1·280	260	1·640	500	1·766
65	1·297	270	1·648	510	1·768
70	1·312	280	1·654	520	1·770
75	1·326	290	1·667	530	1·772
80	1·340	300	1·678	540	1·774
85	1·357	310	1·689	550	1·776
90	1·372	320	1·700	560	1·777
95	1·386	330	1·705	580	1·778
100	1·398	340	1·710	590	1·780
110	1·420	350	1·714	600	1·782
120	1·438	360	1·719		

The *freezing-* and *melting-points* of sulphuric acids of different degrees of concentration are given by Payen in a table quoted in our second edition, p. 133.

A new determination by myself (*Berl. Ber.*, 1881, p. 2649) gave the following results:—

Spec. grav of acid at 15° C.	Freezing-point.	Melting-point.	Spec. grav of acid at 15° C.	Freezing-point.	Melting-point.
1·671	liquid at −20° C.	liquid.	1·767	+ 1°·6	+ 6°·5
1·691	do.	do.	1·790	+ 4°·5	+ 8°·0
1·712	do.	do.	1·807	− 9°·0	− 6°·8
1·727	− 7°·5	− 7°·5	1·822	liquid at − 20° C.	liquid.
1·732	− 8°·5	− 8°·5	1·840	do.	do.
1·749	0°·2	+ 4°·5			

Pickering (*J. Chem. Soc.*, 1890, lvii. pp. 331 *et seq.*) has published an extensive memoir on the freezing-points of sulphuric acid and its solutions. Thilo (*J. Soc. Chem. Ind.*, 1893, p. 827) gives very extended tables as to the results obtained by him in R. Pictet's laboratory. Pictet, himself, subsequently (*Comptes rend.*, cxix. p. 642) supplies the following table:—

Formula	SO_4H_2 per cent.	Spec. grav.	Freezing-point.	Formula.	SO_4H_2 per cent.	Spec. grav.	Freezing-point.
			Degrees.				Degrees.
H_2SO_4	100·00	1·842	+ 10	H_2SO_4 + $15H_2O$	26·63	1·196	− 34
„ + H_2O	84·48	1·777	+ 3	„ 16 „	25·39	1·187	− 26·5
„ $2H_2O$	73·08	1·650	− 70	„ 18 „	23·72	1·170	− 19
„ 4 „	57·65	1·476	− 40	„ 20 „	21·40	1·157	− 17
„ 6 „	47·57	1·376	− 50	„ 25 „	17·88	1·129	− 8·5
„ 8 „	40·50	1·311	− 65	„ 50 „	9·82	1·067	− 3·5
„ 10 „	35·25	1·268	− 88	„ 75 „	6·77	1·045	0
„ 11 „	33·11	1·249	− 75	„ 100 „	5·16	1·032	+ 2·5
„ 12 „	31·21	1·233	− 55	„ 300 „	1·78	1·007	+ 4·5
„ 13 „	29·52	1·219	− 45	„ 1000 „	0·54	1·001	+ 8·5
„ 14 „	28·00	1·207	− 40				

Knietsch (*Ber.*, 1901, p. 4100) gives the following table of the melting-points of sulphuric acid, ordinary and fuming, from 1 per cent. to 100 per cent. SO_3, which I have supplemented by adding the corresponding percentages of H_2SO_4.

SO_3 per cent	H_2SO_4 per cent	Melting-point C.	SO_3 per cent	H_2SO_4 per cent	Melting-point ° C.	SO_3 per cent.	Melting-point ° C.
1	1·22	− 0·6	...		below − 40	82	+ 8·2
2	2·45	− 1·0	...			83	− 0·8
3	3·67	− 1·7	61	74·72	− 40	84	0·2
4	4·90	− 2·0	62	75·95	− 20	85	− 11·0
5	6·12	− 2·7	63	77·17	− 11·5	86	2·2
6	7·35	− 3·6	64	78·40	4·8	87	+ 13·5
7	8·57	− 4·4	65	79·62	− 4·2	88	+ 26·0
8	9·80	− 5·3	66	80·85	+ 1·2	89	+ 34·2
9	11·02	− 6·0	67	82·07	+ 8·0	90	+ 34·2
10	12·25	− 6·7	68	83·39	+ 8·0	91	+ 25·8
11	13·47	− 7·2	69	84·52	+ 7·0	92	+ 14·2
12	14·70	− 7·9	70	85·75	+ 4·0	93	+ 0·8
13	15·92	− 8·2	71	86·97	− 1·0	94	+ 4·5
14	17·15	− 9·0	72	88·20	− 7·2	95	+ 14·8
15	18·37	− 9·3	73	89·42	16·2	96	+ 20·3
16	19·60	− 9·8	74	90·65	− 15·0	97	+ 29·2
17	20·82	− 11·4	75	91·87	34·0	98	+ 33·8
18	22·05	− 13·2	76	93·10 } 99° B.	− 32·0	99	+ 36·0
19	23·27	− 15·2	77	94·83	− 28·2	100	+ 40·0
20	24·50	− 17·1	78	95·05	− 16·5		
21	25·72	− 22·5	79	96·77	− 5·2		
22	26·95	− 31·0	80	98·00	+ 3·0		
23	28·17	− 40·1	81	99·25	+ 7·0		
			81·63	100·00	+ 10·0		

By "melting-point" he understands the temperature at which the cooled acids in which crystals had commenced to form remained constant when the vessel was taken out of the cooling medium during the process of solidification. In a set of curves appended to the original (*cf.* Fig. 51, p. 291) he also shows the temperatures at which the first crystals form and those at which, on cautiously heating, the last crystals were liquefied. The curves show a decided maximum near the point H_2SO_4,H_2O, a minimum at the point $2H_2SO_4,H_2O$, a maximum (nearly coinciding with the first) at the point H_2SO_4, a minimum at $4H_2SO_4,SO_3$, a strong maximum at H_2SO_4,SO_3 (= pyrosulphuric acid), a minimum at $H_2SO_4,2SO_3$, and the highest maximum for SO_3 in the polymerised state.

On *boiling* dilute sulphuric acid, at first nothing but aqueous vapour escapes; according to Graham, acid vapour is mixed with the steam only when no more than 2 mol. of water are present to 1 of SO_3—that is, with a percentage of 84·48 SO_4H_2 or a sp. gr. of 1·78. After several discussions about the loss of sulphuric acid in concentrating it, by Lunge, Bode, Walter, etc., it may be assumed that in manufacturing practice no sensible loss of acid takes place by real *volatilisation* up to a strength of 144° or even of 152° Tw.; but from violently boiling acid there is always a little acid carried away mechanically in the shape of small drops, especially in pans fired from the top and also in the Glover tower, or in a "vesicular state." When the evaporation up to that point takes place quietly at a moderate heat, there is probably no loss of acid at all.

The *boiling-point* of sulphuric monohydrate is stated by Marignac = 338°, by Pfaundler = 317°. The boiling-points of sulphuric acid containing water were examined by Dalton in the beginning of this century. His table, which was obviously wrong, has been replaced by another, founded upon my own investigations (*Berl. Ber.*, xi. p. 370), which is herewith reproduced:—

[TABLES I. AND II.

TABLE I.

Specific gravity.	Temperature. ° C.	Spec. grav. reduced to 15° C	Percentage of SO_4H_2	Boiling-point ° C	Barometer reduced to 0°. Millims
1·8380	17	1·8400	95·3	297	718·8
1·8325	16·5	1·8334	92·8	280	723·9
1·8240	15·5	1·8242	90·4	264	720·6
1·8130	16	1·8140	88·7	257	726·0
1·7985	15·5	1·7990	86·6	241·5	720·1
1·7800	15	1·7800	84·3	228	720·5
1·7545	16	1·7554	81·8	218	726·0
1·7400	15	1·7400	80·6	209	720·6
1·7185	17	1·7203	78·9	203·5	725·9
1·7010	18	1·7037	77·5	197	725·2
1·6750	19	1·6786	75·3	183·5	725·2
1·6590	16	1·6599	73·9	180	725·2
1·6310	17	1·6328	71·5	173	725·2
1·6055	17	1·6072	69·5	169	730·1
1·5825	15	1·5825	67·2	160	728·8
1·5600	17	1·5617	65·4	158·5	730·1
1·5420	17	1·5437	64·3	151·5	730·1
1·4935	18	1·4960	59·4	143	730·1
1·4620	17	1·4635	56·4	133	730·1
1·4000	17	1·4015	50·3	124	730·1
1·3540	17	1·3554	45·3	118·5	730·1
1·3180	17	1·3194	41·5	115	730·1
1·2620	17	1·2633	34·7	110	732·9
1·2030	17	1·2042	27·6	107	732·9
1·1120	17	1·1128	15·8	103·5	732·9
1·0575	17	1·0580	8·5	101·5	735·0

TABLE II.

(Calculated by graphical interpolation.)

Percent SO_4H_2	Boiling-point.	Percent. SO_4H_2.	Boiling-point.	Percent. SO_4H_2.	Boiling-point.	Percent. SO_4H_2.	Boiling-point.
	Degrees.		Degrees.		Degrees		Degrees.
5	101	45	118·5	70	170	86	238·5
10	102	50	124	72	174·5	88	251·5
15	103·5	53	128·5	74	180·5	90	262·5
20	105	56	133	76	189	91	268
25	106·5	60	141·5	78	199	92	274·5
30	108	62·5	147	80	207	93	281·5
35	110	65	153·5	82	218·5	94	288·5
40	114	67·5	161	84	227	95	295

The *tension of aqueous vapour* in sulphuric-acid solutions of various strengths was determined by Regnault in 1845 (*Ann. Chim. anal.* [3], xv. p. 179) for temperatures from 5° to 35° C. We here give his table (for every other degree), adding to the hydrates quoted by him the percentage composition and specific gravities. We also subjoin Sorel's table (p. 312), computed for a wider interval of temperatures, better suited for the wants of sulphuric-acid manufacture. The tensions are stated in millimetres of mercurial pressure.

Regnault's Table of the Aqueous-Vapour Tensions of Dilute Sulphuric Acid

C.	H_2SO_4 + H_2O 84·5 % 1·780 mm	H_2SO_4 + 2 H_2O 73·1 % 1·654 mm	H_2SO_4 + 3 H_2O 64·5 %. 1·554 mm.	H_2SO_4 + 4 H_2O 57·6 %. 1·477. mm.	H_2SO_4 + 5 H_2O 52·1 %. 1·420. mm.	H_2SO_4 + 7 H_2O 43·7 %. 1·340 mm.	H_2SO_4 + 9 H_2O 37·7 %. 1·287. mm.	H_2SO_4 + 11 H_2O 33·1 %. 1·247. mm.	H_2SO_4 + 17 H_2O 24·3 %. 1·176. mm.
5	0·105	0·388	0·861	1·294	2·137	3·168	4·120	4·428	5·478
7	0·108	0·430	0·985	1·510	2·464	3·643	4·728	5·164	6·300
9	0·112	0·476	1·125	1·753	2·829	4·176	5·408	5·980	7·216
11	0·118	0·527	1·280	2·025	3·240	4·773	6·166	6·883	8·237
13	0·124	0·586	1·454	2·331	3·699	5·443	7·013	7·885	9·374
15	0·131	0·651	1·648	2·674	4·215	6·194	7·958	8·995	10·641
17	0·139	0·725	1·865	3·059	4·793	7·036	9·014	10·222	12·054
19	[illegible]	0·808	2·108	3·492	5·440	7·980	10·191	11·583	13·628
21	0·159	0·901	2·380	3·977	6·166	9·039	11·506	13·090	15·383
23	0·171	1·006	2·684	4·523	6·979	10·226	12·974	14·760	17·338
25	0·184	1·125	3·024	5·135	7·892	11·557	14·613	16·610	19·516
27	0·199	1·258	3·405	5·822	8·914	13·050	16·413	18·659	21·944
29	0·216	1·408	3·830	6·594	10·060	14·723	18·485	20·929	24·650
31	0·235	1·557	4·305	7·459	11·345	16·600	20·765	23·443	27·666
33	0·256	1·767	4·838	8·432	12·785	18·704	23·311	26·228	31·025
35	0·280	1·981	5·432	9·524	14·400	21·063	26·152	29·314	34·770

Knietsch (*Berl. Ber.*, 1901, p. 4111) has also determined the vapour-tensions of sulphuric acid, both ordinary and fuming, at various temperatures up to 100° C. As may be imagined, the aqueous-vapour pressures decline rapidly with the concentration of the ordinary acid, and for acids from 90 to 98·6 per cent. they are = 0 even at 100°. From this point the vapour-tension, now of course produced by SO_3, rises very rapidly, as is shown by the following table, where

Tension of Aqueous Vapour in Mixtures of Sulphuric Acid and Water (Sorel).

Spec. grav. of Acid.	Approx. degree, Twaddell.	Per-cent. of H_2SO_4.	Temperatures (° C.).																	
			10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95
			mm.	mm.	mm.	mm.	mm.	mm.	mm	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
1·342	68½	44	4·4	6·1	8·5	11·5	15·5	20·9	28·1	37·4	48·3			...	...	...	...	...	...	...
1·361	72	46	4·0	5·5	7·7	10·5	14·5	19·7	26·3	33·6	44·4	59·6	76·5	96·4	...	...			...	
1·380	76	48	3·7	5·0	7·1	9·6	13·4	18·1	23·9	30·5	40·1	53·5	69·0	86·8	107·2	132·1		..	...	...
1·399	80	50	3·3	4·5	6·5	8·8	12·0	16·4	21·4	27·4	35·9	47·4	61·3	77·0	95·6	118·1	152·0	192·6	236·7	...
1·418	83½	52	3·0	4·0	5·8	7·9	10·9	14·5	18·9	24·1	31·5	41·5	54·0	67·9	84·5	104·5	131·2	166·5	207·9	251·5
1·439	88	54	2·6	3·6	5·0	7·0	9·5	12·5	16·5	21·3	27·8	36·2	47·2	59·9	74·8	92·6	116·1	146·8	183·5	222·0
1·459	92	56	2·2	3·1	4·3	6·0	8·1	11·0	14·2	18·5	24·1	31·0	41·6	51·6	65·0	80·6	100·9	128·2	160·0	195·0
1·480	96	58	1·9	2·6	3·5	5·1	7·2	9·1	12·0	15·8	20·4	26·1	34·5	44·0	55·4	68·4	86·2	110·6	138·5	169·5
1·502	100½	60	1·6	2·1	3·0	4·3	6·1	7·5	10·0	13·0	16·9	21·6	28·7	36·7	46·1	56·7	72·3	94·0	118·7	146·0
1·525	105	62	1·4	1·8	2·6	3·6	5·0	6·5	8·1	10·5	13·9	17·7	23·9	30·0	37·7	46·2	59·7	78·2	100·7	125·0
1·547	109½	64	1·2	1·6	2·2	3·0	4·0	5·5	6·5	8·2	10·9	14·0	18·7	23·9	30·3	37·4	48·0	63·8	83·7	105·0
1·569	114	66	1·1	1·4	1·8	2·5	3·5	4·5	5·4	6·5	8·9	11·5	15·2	19·1	24·2	30·3	39·0	52·5	70·0	88·0
1·592	118½	68	0·9	1·2	1·5	2·1	3·0	3·8	4·5	5·4	7·2	9·5	12·3	15·4	19·4	24·4	31·4	42·5	56·0	72·0
1·615	123	70	0·8	1·0	1·3	1·8	2·5	3·3	3·8	4·4	5·9	7·5	9·5	12·1	15·5	19·8	25·5	33·9	44·4	57·0
1·638	127½	72	0·7	0·8	1·0	1·4	2·0	2·8	3·2	3·6	4·8	6·0	7·5	9·5	12·0	15·4	20·0	26·2	33·7	43·4
1·662	132½	74	0·5	0·6	0·6	1·2	1·7	2·1	2·6	3·1	3·9	4·9	6·0	7·5	9·5	12·1	15·4	19·5	24·5	31·5
1·687	137½	76	0·4	0·4	0·5	1·0	1·4	1·8	2·1	2·5	3·0	4·0	4·8	5·9	7·5	9·5	11·8	15·0	18·5	22·0
1·710	142	78	0·3	0·3	0·4	0·8	1·1	1·4	1·7	2·1	2·4	3·0	3·5	4·0	5·7	7·0	8·5	10·5	13·0	15·8
1·733	146½	80	0·2	0·2	0·3	0·6	0·8	1·1	1·3	1·6	1·9	2·4	2·9	3·3	4·1	5·0	6·2	7·5	9·3	11·0
1·755	151	82	0·1	0·1	0·2	0·4	0·5	0·5	0·9	1·1	1·4	1·7	2·0	2·3	2·7	3·2	3·9	4·7	5·6	6·8

the pressure of ¾ vol. fuming acid + ¼ vol. air is expressed in atmospheres.

Temp.	SO_3 30 per cent.	SO_3 40 per cent.	SO_3 50 per cent.	SO_3 60 per cent.	SO_3 70 per cent.	SO_3 80 per cent	SO_3 100 per cent
C.	Atm.	Atm.	Atm.	Atm.	Atm.	Atm.	Atm.
35	..	.	...	...	...	0·150	0·400
40	...	0·075	...	0·225	0·375	0·500	0·650
45	0·050	0·125	...	0·350	0·575	0·650	0·875
50	0·100	0·175	0·350	0·525	0·775	0·875	1·200
55	0·140	0·225	0·450	0·675	1·025	1·200	1·600
60	0·200	0·275	0·550	0·825	1·400	1·500	1·850
65	0·225	0·350	0·700	1·025	1·650	1·900	2·250
70	0·275	0·400	0·825	1·275	2·050	2·300	2·725
75	0·340	0·475	1·000	1·570	2·525	2·800	3·300
80	0·400	0·575	1·150	1·850	3·100	3·500	4·000
85	0·450	0·675	1·400	2·150	3·700	4·175	4·900
90	0·530	0·825	1·700	2·575	4·400	5·050	5·900
95	0·625	0·950	2·050	3·150	5·200	6·000	.
100	0·730	1·000	2·400	3·700	6·000	..	...

E. Briggs (*J. Soc. Chem. Ind.*, 1903, p. 1275) describes his experiments on the vapour-tensions of mixtures of sulphuric acid and water, which he applies to the construction of the following table, the figures denoting millimetres of mercury :—

Percentage of H_2SO_4	Temperature (°C).												
	100	110	120	125	130	140	150	160	170	175	180	190	200
[illegible]	[illegible]	42·5	[illegible]	90·8	112·5	168·5	300·0	...	...	...	...	...	.
79·17	14·3	33·8	56·2	67·5	86·2	132·0	210·0	335·0	..	.	...	...	...
81·81	8·5	18·8	32·5	40·0	51·5	75·5	126·5	207·5	322·5	400	...	...	..
84·26	5·3	11·1	18·5	23·1	29·5	46·0	76·5	118·5	180·0	230	282·5	...	...
87·32	2·4	5·0	8·7	10·5	15·0	26·3	43·5	63·8	92·5	113	132·5	191·0	367
91·22	.	...	...	5·0	6·9	10·0	15·0	25·0	40·6	51	62·0	92·5	149

B. C. Burt (*J. Chem. Soc.*, 1904, lxxxv. pp. 1339 *et seq.*) describes his experiments on the vapour pressure of sulphuric-acid solutions, carried on by means of a specially designed apparatus, for concentrations ranging between 24·92 and 95·94 per cent. SO_4H_2, and he also reviews all the earlier work on this subject. His conclusion is that, in solution, combination ensues between sulphuric acid and water with the formation of new compounds. There is no evidence to show that definite hydrates exist in the solutions; in fact, several attempts to calculate molecular weights, presupposing the existence of certain hydrates, led to very contradictory results.

The *specific heat* of monohydrated sulphuric acid at 16° to 20° C. is 0·3315 (water = 1). Marignac states the specific heat of acid diluted with water as follows:—

H_2SO_4 + 5 aq. = 0·5764
" + 10 " = 0·7212
" + 15 " = 0·7919
" + 25 " = 0·8537
" + 50 " = 0·9155
" + 100 " = 0·9545
" + 200 " = 0·9747
" + 400 " = 0·9878

The following table, by Bode, is more convenient for practical use (*Z. angew. Chem.*, 1889, p. 244):—

Spec grav.	Spec. heat.	Spec. grav.	Spec. heat.
1·842	0·3315	1·020	0·67
1·774	0·38	1·263	0·73
1·711	0·41	1·210	0·78
1·615	0·45	1·162	0·82
1·530	0·49	1·116	0·87
1·442	0·55	1·075	0·90
1·383	0·60	1·037	0·95

Cf. also Pickering (*J. Chem. Soc.*, lvii. p. 90).

Knietsch (*Berl. Ber.*, 1901, p. 4102) gives the specific heats of acids of higher concentration and fuming acids up to 100 per cent. anhydride. The curve (Fig. 51, p. 291) falls continuously with the concentration, till 20 per cent. SO_3 is reached; it then rises again, and at 100 per cent. SO_3 reaches the considerable amount of 0·77. The principal points are:—

Total SO_3	Free SO_3.	Specific heat.	Total SO_3.	Free SO_3.	Specific heat
80	...	0·3574	92	56·45	0·400
82	2·0	0·345	94	67·34	0·455
84	12·89	0·340	96	78·23	0·535
86	23·78	0·340	98	89·12	0·650
88	34·67	0·350	100	100	0·770
90	45·56	0·360			

The exponents of *refraction* of sulphuric acid have been determined by Veley and Manley (*Roy. Soc. Proc.*, lxxix. 1905, pp. 469-487).

Chemical Behaviour of Sulphuric Acid.

On mixing oil of vitriol with water a considerable rise of temperature takes place, water being chemically fixed by the formation of certain hydrates, as described above. Besides, on mixing concentrated acid with water, as already mentioned, a not inconsiderable contraction takes place, which must equally lead to an evolution of heat. But on mixing strong sulphuric acid with *snow* excessive cold is produced by the heat becoming latent on the liquefaction of snow, which considerably exceeds that becoming free in consequence of the chemical combination. This cold, however, is only produced when the proportion between acid and ice does not exceed certain limits: for 1 part of sulphuric acid there must be 1¼ parts of snow present; with less snow, there is a rise of temperature.

Even when sulphuric acid is more strongly diluted much heat is liberated. Many observers have worked upon this subject; but we quote here only a few. Thomsen (*Deutsch. chem. Ges. Ber.*, iii. p. 496) states that 1 g.-mol. (that is 98 g.) H_2SO_4 gives the following amounts of heat when combining with x molecules of water:—

x.	
1	6272 metrical heat-units
2	9364 „ „
3	11108 „ „
5	13082 „ „
9	14940 „ „
19	16248 „ „
49	16676 „ „
99	16850 „ „
199	17056 „ „
499	17304 „ „
799	17632 „ „
1599	17848 „ „

Somewhat higher results were obtained by Pickering (*J. Chem. Soc.*, lvii. p. 94).

Knietsch (*Berl. Ber.*, 1901, p. 4103) gives the following figures of the heat of dissolution, found both in the laboratory and by large scale experiments with 400 kg. water (for the values of fuming acid, see p. 284):—

SO_3 per cent.	H_2SO_4 per cent.	Calories	SO_3 per cent.	H_2SO_4 per cent.	Calories.
50	61·25	39	67	82·08	93
51	62·48	41	68	83·30	98
52	63·70	44	69	84·53	103
53	64·93	46·5	70	85·75	108
54	66·15	49	71	86·98	113
55	67·38	51·5	72	88·20	119
56	68·60	54	73	89·43	126
57	69·83	57	74	90·65	133
58	71·05	59·5	75	91·88	139
59	72·28	62	76	93·10	146
60	73·50	65	77	94·33	152
61	74·73	68	78	95·55	160
62	75·95	72	79	96·78	168
63	77·18	75	80	98·00	178
64	78·40	79	81	99·23	188
65	79·63	83·5	81·63	100·00	193
66	80·85	88			

The curve both for ordinary and fuming acid runs on quite steadily, without any breaks, so that the formation of the different hydrates evidently does not cause any special evolution of heat.

On account of this considerable evolution of heat, concentrated sulphuric acid and water must always be mixed with care: the water ought never to be poured into the acid, but the acid run in a thin jet into the water with constant stirring. In case of a sudden mixture, so much heat is liberated at once that the acid may be raised to the boiling-point and splash about; and glass vessels are easily cracked thereby.

H. Howard (*J. Soc. Chem. Ind.*, 1910, pp. 3-4) describes a method for estimating the strength of fuming sulphuric acid by the rise of temperature on dilution with water.

The affinity of sulphuric acid for water is also proved by its great hygroscopicity. Concentrated sulphuric acid is one of the best means of drying gases; and it is not only used in this way for innumerable scientific, but also for some technical purposes —for instance, in the manufacture of chlorine by Deacon's process, where the gaseous mixture, having been deprived of its hydrochloric acid by water, is passed through a coke-tower fed with sulphuric acid, in order to be deprived of its moisture. In the same way, chlorine gas is dried for the process of utilising tinned scrap-iron by treatment with chlorine, which in the dry state does not act upon iron, but gives with tin anhydrous tin tetrachloride. On the large scale, usually not the most highly concentrated acid, but acid of about 80 per cent. H_2SO_4, is employed for drying gases, but care must be taken lest its concentration during the work should not rank below sp. gr. 1·72, as it would then not act as dehydrator.

Concentrated sulphuric acid acts also upon liquid and solid bodies by depriving them of water or even splitting off the elements of the same if the substance only contains the latter, but no readily formed water. Upon this action, too, a host of scientific and technical applications of sulphuric acid are founded. In this case frequently the so-called *sulphonic acids* are formed, generally compounds easily lending themselves to further reactions. Instances of this are—the formation of ether by the splitting-up of sulphuric acid, with the intermediate formation of sulphovinic acid; that of ethylene on the further splitting off of water; the preparation of nitrobenzene, picric acid, nitronaphthalene; the manufacture of resorcine and alizarine by the alkaline fusion of the sulphonic acids of benzene and anthraquinone; and many other cases.

The charring of many organic substances, such as wood, sugar, etc., by contact with strong sulphuric acid, proceeds from the same source. Necessarily this acid, in its concentrated form, must have an extremely prejudicial effect on the animal body. The remedy usually applied, viz., burnt magnesia, cannot do much good when the epithelium of the œsophagus and the stomach has been destroyed.

The affinity of concentrated sulphuric acid for water is also shown by the fact that it easily runs over, when kept in open vessels, by attracting moisture from the air—a fact to be remembered in the case of employing it for keeping balances, etc., dry.

Decompositions of Sulphuric Acid.—Some of these have been mentioned already—for instance, that into anhydride and water by evaporation. The mixed vapour, on account of the unequal velocity of diffusion of the two vapours, can be separated to a great extent into its two constituents, so that at 520° C., within an hour, a residue of 60 per cent. monohydrate and 40 per cent.

anhydride, at 445° C. 75 per cent. monohydrate and 25 per cent. anhydride was obtained (Wanklyn and Robinson, *Roy. Soc. Proc.*, xii. p. 507). Perhaps a process for preparing fuming acid can be founded upon this fact. Even far below the boiling-point the dissociation begins in the liquid acid. It has been pointed out that already at 30° to 40° C. the monohydrate begins to give off vapours of anhydride (Marignac), which fact has been confirmed by the exact researches of Dittmar (*Chem. Soc. J.* [2], vii. p. 446) and Pfaundler and Polt (*Z. f. Chemie*, xiii. p. 66).

A more thorough decomposition into sulphur dioxide, oxygen, and water takes place on conducting the vapour of sulphuric acid through porcelain or platinum tubes filled with chips of porcelain and heated to a bright red heat. This mode of decomposition has been recommended by Deville and Debray as a "cheap" plan for making oxygen; but it does not seem to have answered, owing to the insufficient sale of sulphurous acid or its salts; it was expected to play a great part in the manufacture of anhydride by Winkler's process, but even for this purpose it has not been found economical.

On heating with charcoal to 100° or up to 150° C., sulphuric acid yields carbon dioxide and sulphur dioxide; on boiling with phosphorus, sulphur; on boiling with sulphur, sulphur dioxide; by the action of the electric current, hydrogen, oxygen, sulphur, etc. (in dilute sulphuric acid the electric current merely causes the decomposition of water).

Sulphuric acid at temperatures below its boiling-point behaves as the strongest of all acids, and expels all other acids from their salts when the solubilities, etc., allow this; but, inversely, sodium sulphate is also decomposed by hydrochloric acid. In fact, the "avidity" of hydrochloric and nitric acid at ordinary temperatures much exceeds that of sulphuric acid. Boussingault (*Ann. Chim. Phys.* [5], ii. p. 120) has shown that dry hydrochloric acid gas at a red heat decomposes the sulphates of sodium, potassium, barium, strontium, and calcium (see further on). More refractory acids expel sulphuric acid at higher temperatures—for instance, boric acid, silica, and phosphoric acid.

With the bases sulphuric acid forms two principal series of salts, viz., acid salts, of the formula $SO_2\diagup\begin{smallmatrix}OH\\OM\end{smallmatrix}$, and neutral salts, of the formula $SO_2 <^{OM}_{OM}$. Very frequently it also forms basic salts, rarely hyperacid salts.

The technical applications of sulphuric acid to a great extent rest on its great affinity to all bases. The acid and neutral salts are soluble in water, excepting the neutral salts of barium, strontium, lead, silver, and mercury (in the state of protoxide), which are little or not at all soluble in water and dilute acids. Calcium sulphate is sparingly soluble in water. Most sulphates are insoluble in alcohol. The basic sulphates are mostly insoluble in water, but soluble in acids. The sulphates incline very much towards the formation of double salts, of which those are called *alums* which contain a combination of univalent and trivalent (corresponding to a double atom of quadrivalent) metals.

The neutral salts of the alkali-metals, of calcium, magnesium, silver, manganese, and ferrosum, the latter only if entirely free from acid and peroxide (a condition very rarely realised), do not redden blue litmus-paper, whilst all other soluble sulphates do this.

On heating to a red heat, only the neutral sulphates of the alkalies, of the alkaline earths, and of lead remain unchanged. At a still higher temperature (that of melting iron) the two latter classes are also decomposed, but the alkaline sulphates are volatilised without a change. Even zinc sulphate and manganous sulphate are not easily decomposed. This explains the difficulty of completely converting blende into oxide of zinc.

On roasting, the decomposable sulphates yield metallic oxides, sulphur dioxide, and oxygen. They are much more easily split up on heating with certain additions, such as coal, iron, etc.

On the *metals* sulphuric acid acts in a very different way. The water-decomposing metals in the cold yield nothing but hydrogen with it; at high temperatures even zinc and iron already yield sulphurous acid; and zinc, if certain conditions are observed, can even yield sulphuretted hydrogen (Fordos and Gélis).

Most of the heavy metals do not act upon sulphuric acid in the cold and in a dilute state (they yield sulphur dioxide only on being heated with *concentrated* acid), such as arsenic, antimony, bismuth, tin, lead, copper, mercury, silver (sulphates being formed at the same time); gold, iridium, and rhodium do not act on sulphuric acid at any temperature.

Pure sulphuric acid has a very slight action on *platinum*, even at its boiling-point, and hardly any action at lower temperatures, but the action is increased by the impurities never absent from commercial acid. Impure platinum may also be acted upon to some extent, but the action on gold is *nil*. We shall go into this subject when treating of the concentration of sulphuric acid in platinum vessels.

The behaviour of *cast-iron* towards sulphuric acid is of great technical importance. It has been known for many years past that concentrated oil of vitriol acts very little indeed upon cast-iron, whether hot or cold, provided the access of air is excluded, the moisture from which would dilute the acid and cause it to act more strongly. It was, however, at first considered an extremely bold step when Lancashire alkali-makers began to decompose common salt with sulphuric acid in cast-iron pots, as is mentioned in our second volume, in the chapter treating of the manufacture of saltcake.

Since that period manufacturers have become much bolder, and for many years past cast-iron vessels have been employed for "parting" alloys of silver and gold by boiling sulphuric acid, for making nitrobenzene and analogous products by a mixture of strong sulphuric and nitric acid, and innumerable other purposes where strong acids have to be manipulated either hot or cold, even for the last concentration of sulphuric acid itself. Dilute sulphuric acid, if the dilution be not too strong, acts very little on cast-iron in the cold or at a gentle heat, if air be excluded; it can therefore be employed for "acid eggs," in which chamber-acid is forced up, in lieu of pumps, and similar purposes.

It is usually assumed that some descriptions of cast-iron resist the attack of acids more than others. This point, together with some others of importance, has been the subject of experiments by myself and collaborators (*Chem. Ind.*, 1886, p. 74).[1]

These experiments lead to the following conclusions:—

(1) At the ordinary temperature all acids down to 106° Tw.

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[1] A full report is also given in the second edition of this book, pp. 141-143.

act very little on all descriptions of cast-iron, if the access of air is prevented.

(2) At 100° C. the action is much stronger. It is least in the case of acid of 168° Tw., 1½ times stronger with acid 142° Tw., and 3 times stronger with acid 106° Tw.

(3) At the boiling-point of the acids the differences are far more pronounced. Acid of 168° Tw. acts very little even then (*i.e.*, at 295° C.), both in the pure state, or as commercial acid (containing a little N_2O_3), or when containing a little SO_2. But acid of 142° Tw. acts (on an average) 14 times stronger at its boiling-point = 200° than the same acid at 100° C., and 20 times stronger than acid of 168° Tw. At 200° C. commercial acid of 142° Tw. does not act very differently from pure acid of the same strength. Hence it is not feasible to concentrate acid of 142° to higher strengths in iron vessels; only from 168° Tw. upwards the acid can be boiled in cast-iron vessels. Acid of 106° Tw. at its boiling-point (= 147° C.) acts rather less than acid of 142° Tw. at 200° C., but still 14 times as much as acid of 168° Tw. at 295° C. There is no difference between pure and commercial acid in this case.

(4) The differences between various mixtures of cast-iron are of no importance against acid of 168° Tw. in all cases, and against the weaker acids at 20° and 100° C. But the latter acids at their boiling-point act decidedly less on charcoal-pig and on chilled cast-iron than on all other kinds. A difference between hot and cold casting could not be found. The strongest attack took place on Scotch pig and on mixtures containing such.

In another series of tests we examined the action of *monohydrated sulphuric acid* on various metals, both on standing six days at 20° and on heating two hours to 100° C., always with exclusion of air. The loss of weight was:—

	Loss per cent.		Loss in grammes per square centimetre of surface.	
	6 days at 20° C.	2 hours at 100° C.	6 days at 20° C.	2 hours at 100° C.
Cast-iron . .	0·041	0·071	0·062	0·015
Wrought-iron .	0·175	0·313	0·056	0·095
Copper . .	2·630	excessive	1·115	excessive
Lead . . .	3·480	3·650	1·790	1·847

Knietsch (*Ber.*, 1901, p. 4109) gives the following table respecting the action of sulphuric acid (ordinary and fuming) of various strengths on cast-iron, mild steel ("Flusseisen"), and puddled iron. The cast-iron contained 2·787 per cent. graphite and 3·55 per cent. total carbon, the mild steel 0·115 per cent. carbon, and the puddled iron 0·076 per cent. The figures denote the loss of the metal per superficial metre and hour in grammes, after treating with acid for seventy-two hours at 18° to 20° C., with exclusion of air.

H_2SO_4 per cent.	SO_3 per cent	Cast-iron.	Mild steel.	Puddled iron.
48·8	39·9	0·2177	...	..
61·2	50·0	0·1510	...	0·3032
67·7	55·3	0·0847	...	0·0789
73·4	59·9	0·0662	...	0·0623
79·7	65·0	0·1560	..	0·1159
83·7	68·4	0·1388	...	0·1052
85·1	69·5	0·1306	.	0·1034
88·2	72·0	0·1636	.	0·1417
90·6	73·9	0·1760	...	0·1339
92·0	75·2	0·0983	...	0·1040
93·0	75·9	0·0736	0·0987	0·0855
94·3	77·0	0·0723	0·0987	0·0708
95·4	77·9	0·1274	0·0933	0·1209
96·8	79·0	0·1013	0·0815	0·0988
98·4	80·3	0·0681	0·0533	0·0655
98·7	80·6	0·0589	0·0509	0·0570
99·2	81·0	0·0568	0·0418	0·0504
99·30	81·07	0·057	0·042	0·050
99·50	81·25	0·060	0·038	0·049
99·77	81·45	0·066	0·042	0·049
100·00	81·63	0·087	0·088	[illegible]
total SO_3	free SO_3			
81·8	0·91	0·201	0·393	0·323
82·02	2·00	0·190	0·285	0·514
82·28	3·64	0·132	0·441	0·687
82·54	4·73	0·154	0·956	1·075
82·80	7·45	0·151	0·566	1·321
83·50	10·17	0·079	0·758	1·540
84·20	12·89	0·270	1·024	0·892
84·62	16·16	0·271	1·400	0·758
85·05	18·34	0·076	1·988	1·530
86·00	23·78	0·070	0·245	0·471
88·24	34·67	0·043	0·033	0·053
90·07	45·56	0·040	0·018	0·019

Knietsch (*loc. cit.*, p. 4090) make the following further remarks on this subject. Whereas *cast-iron* vessels are very suitable for the manufacture of hydrated sulphuric acid, this is not the case for fuming acids, for these, although they corrode the metal but slightly, cause it to crack, sometimes quite suddenly, with a loud report. Evidently the fuming acid penetrates into the pores of the metal, where it is reduced to SO_2 and H_2S, with formation of CO_2 from the carbon of the cast-iron—all of them gases with somewhat low critical temperatures which produce high tensions in the interior of the metal.

Föhr (*Fischer's Jahresber.*, 1886, p. 295) points out that cast-iron, in order to resist acids, ought to possess much chemically combined and little graphitoidal carbon, whilst precisely the opposite holds good with reference to resistance against alkali, as in caustic-pots and the like. In the former case the iron ought to contain much manganese and little silicon, in the latter little manganese and much silicon. Fusing alkalies dissolve combined carbon and manganese, but very little graphite or silicon [?]. A mixture which makes good decomposing-pans (or acid concentrating-pans) would make bad caustic-pots, and *vice versâ.*

Ricevuto (*Chem. Zeit.*, 1907, p. 960) found a cast-iron dish, which resisted the action of acids particularly well, to contain 9·24 per cent. Si, 0·526 per cent. P, 0·080 S. This dish had been supplied by Hartmann and Benker.

Sometimes ferro-silicon (up to 10 per cent.) is employed to make cast-iron acid-proof, whereas 1 per cent. nickel makes it proof against alkali (Guttmann, *J. Soc. Chem. Ind.*, 1908, p. 668).

Wrought-iron is much more acted upon than cast-iron by weaker acids, as appears from some of the above-quoted investigations, but at the ordinary temperature it resists the action of strong sulphuric acid down to 140° Tw., and probably even a little below that strength. Where, however, through the action of moist atmospheric air, the acid gets more diluted, a very strong action sets in. Hence the wrought-iron vessels in which sulphuric acid is now very generally carried must be protected inside against any access of air when empty; and at the manholes, etc., where temporary access of air is unavoidable, they are best protected by a sheet of lead.

By *fuming acids* wrought-iron (and zinc), according to Knietsch, *loc. cit.*, is somewhat strongly acted upon in case of acids containing up to 27 per cent. SO_3; this is explained by the increase of electric conductivity, apparent from the curve No. 5, Fig. 51, p. 291. We notice that the minimum lies at 100 per cent. H_2SO_4: then the conductivity rises sharply, the maximum being at 10 to 15 per cent. free SO_3, whereupon it sinks just as rapidly to a minimum. At 27 per cent. free SO_3, wrought-iron is again entirely passive, and apparatus made of it may serve for many years for the manufacture of high-strength fuming acids.

The action of sulphuric acid on lead has been the subject of many experiments. Calvert and Johnson (*Comptes rend.*, lvi. p. 140) came to the conclusion that lead is all the more acted upon the purer it is, and that an energetic action only takes place by acid above the sp. gr. of 140° Tw. Similar results were obtained by Mallard (*Bull. Soc. Chem.*, 1874, ii. p. 114) and Hasenclever.

Bauer (*Berl. Ber.*, 1875, p. 210) found that 50 g. of strongest oil of vitriol (168° Tw.) with 0·2 g. of pure lead produced a sensible evolution of gas at 175°, stronger at 196°; at 230° to 240° suddenly all the lead is changed into sulphate, with formation of SO_2, H and S. Lead containing varying quantities of bismuth (0·71 or 4 or 10 per cent.) was even more strongly acted upon, whilst small quantities of antimony and copper make the lead more resisting; platinum acts in a similar way. Lead containing 10 per cent. tin behaves like pure lead.

According to experiments made by J. Glover (*Chem. News*, xlv. p. 105), pure lead is less acted upon when suspended in a vitriol chamber than lead containing 0·1 to 0·75 per cent. copper, or 0·1 to 0·5 per cent. antimony. N. Cookson (*ibid.*, p. 106) found that strong acids at a high temperature act more upon lead containing antimony than upon pure lead, whilst weaker acid at a lower temperature acts the other way. *Cf.* also Mactear (*Chem. News*, xli. p. 236).

In the north of England those rolling-mills which sell the sheet-lead to the vitriol-works, supply a special kind of "chemical lead" which is made from the melted-up old chamber-lead, pipes, etc.; in this case many impurities, especially antimony, from "regulus"-valves, etc., get into the lead, which are supposed to improve its quality for acid-chambers.

Hochstetter (*Bull. Soc. Ind. du Nord*, 1890, p. 231) found that lead absolutely free from copper is strongly acted upon by sulphuric acid, and that as little as 0·02 per cent. Cu protects it, as well as antimony. His results are based entirely on experience made on the large scale, and they were not controlled by ascertaining any loss of weight.

Napier and Tatlock (*Chem. News*, xlii. p. 314) found that the action of sulphuric acid on lead at the ordinary temperature is accompanied by an evolution of hydrogen, which may cause bulging out of the closed lead vessels in which the acid is sometimes sent out for sale.

The experiments of Veley (*J. Soc. Chem. Ind.*, 1891, p. 211), according to which mixtures of nitrous and nitric acid have a stronger action on lead than either acid by itself, have no practical bearing on the behaviour of the acid in vitriol chambers, since, if nitric acid occurs there, it is always accompanied by nitrous acid, and, what is far more important, the immense excess of sulphuric acid greatly modifies all conditions of the case.

An extensive investigation on the action of sulphuric acid on lead made by myself together with E. Schmid has been published in *Z. angew. Chem.*, 1892, p. 642, also partly in *J. Soc. Chem. Ind.*, 1891, p. 146. I here give a very brief summary of our results, some of which are of great practical importance.

1. *At higher temperatures* the *purest* lead in all cases resists both pure and nitrous sulphuric acid, with or without access of air, much better than "regulus metal" (82 Pb, 18 Sb) or "hard lead" (1·8 per cent. Sb), or even soft lead with only 0·2 per cent. Sb. *In the cold*, lead with 0·2 per cent. Sb. is very slightly superior to the purest lead; regulus metal behaves much worse, and hard lead worst of all.

2. *Concentrated nitrous vitriol* is always more active than pure acid. In the case of somewhat dilute acid (sp. gr. 1·72 to 1·76), nitrous vitriol acts less than pure acid on soft lead and hard lead, owing to a protective coating of lead sulphate being formed. If the acid is more dilute, the action is again stronger (*cf.* below). In all cases nitrous vitriol acts more in the presence than in the absence of air.

3. Comparing two samples of soft lead, the purer sample was found decidedly better; even a very slight proportion of bismuth (0·044 per cent.) acts injuriously.

4. It is altogether inadmissible to judge of the resistance of

lead to sulphuric acid from the quantity of the *gas* (hydrogen) evolved. Soft lead gives off at the ordinary temperature, after a week's contact, much gas; hard lead, although losing much more weight, very little gas ($\frac{1}{200}$ of the theoretical quantity), probably owing to galvanic action. On this account, if sulphuric acid is to be sent out in tightly-closed or soldered-up leaden boxes, they should not be made of soft, but of hard lead, since otherwise the hydrogen may bulge up or burst the vessels.

5 (*a*). Lead containing up to 0·2 per cent. *copper* (alloys containing more copper cannot be homogeneously rolled (is *in the cold* acted upon by strong sulphuric acid more than pure lead; with nitrous acid there is not much difference. At 100° C. all kinds of acid act in the same way on pure lead and on lead containing copper; concentrated pure acid rather less than concentrated nitrous vitriol, but more than nitrous vitriol of sp. gr. 1·72 (*cf.* No. 2). At 200° C., concentrated acid acts alike on pure lead and on lead containing 0·02 per cent. Cu; lead containing more copper is slightly less acted upon by pure acid, but rather more by nitrous vitriol.

(*b*) Above 200° (225° to 255°) lead alloyed with 1 per cent. *antimony* is far more strongly acted upon than pure lead (in the proportion of 26·5 to 1 at 225°); but lead containing 0·2 per cent. *copper* resists the acid at 235° much *better* than pure lead in the proportion of 1 : 17, and at 255° in the proportion of 1 : 26·5.

6 (*a*). Pure soft lead gives no visible evolution of gas with pure concentrated sulphuric acid up to 220°. From this point more gas-bubbles are continually given off, and at 260° the lead is momentarily dissolved with strong frothing, smell of SO_2, and precipitation of sulphur, the temperature rising to 275°.

(*b*) The same lead, alloyed with 0·2 per cent. of copper, shows a visible evolution of gas only at 260°, regularly increasing up to the boiling-point (310°), at which the lead is very gradually dissolved.

(*c*) Soft lead, alloyed with 1 per cent. Sb, gives with sulphuric acid the first visible gas at 175°, more strongly at 225°, and between 275° and 280° there is the same turbulent, sudden solution as in the case of pure soft lead. [Bauer, *Berl. Ber.*, 1875, p. 210, found similar results; according to him 0·73 per cent. *bismuth* lowers the temperature of sudden decomposition from 240° to 160°.] .

Hence the purest lead is subject to instantaneous solution by sulphuric acid at 260°. An addition of 1 per cent. Sb raises this temperature only about 20°, but 0·2 per cent. Cu completely destroys this liability to sudden decomposition.

7. The percentage of *oxygen* in lead is very slight even in extreme cases, and does not seem to have any connection with its liability to be acted upon by acid. But that liability, as may be imagined, is less when the *density of the surface* is *mechanically* increased.

8. The final considerations in selecting the kind of lead best suited for constructing apparatus for the manufacture of sulphuric acid are as follows:—

For vitriol-chambers, towers, tanks, pipes, and all other instances where the temperature can rise but moderately, and certainly never up to 200° C., the purest soft lead is preferable to every other description of lead, being least acted upon by hot acid, whether dilute or concentrated, pure or nitrous.

Any sensible proportion of *antimony* is in nearly all cases *injurious; copper* causes at least no improvement. This, of course, does not apply to those cases where the lead requires an addition to its tensile strength, nor to that mentioned *sub* No. 4 of packages for acid to be closed air-tight. Hence an addition of about 0·2 per cent. antimony may be useful in the case of apparatus which is only in contact with *cold* acid; but with *warm* acid even this percentage is to be avoided.

For *very high temperatures*, e.g., *the hottest boiling-down pans*, which ought not to be heated above 200° C., but may sometimes be raised to that point, *an addition of 0·1 to 0·2 per cent. copper* is *advantageous*, while antimony should be avoided here under all circumstances (*cf.* No. 6*b*). That percentage of copper has no action at 200°, but only above 220°; and in the presence of bismuth it protects the lead from the sudden destruction sometimes observed.

9. Technical "*sulphuric monohydrate*" at 50° C. *acts far more strongly on lead than concentrated sulphuric acid.* [The "monohydrate" employed in our experiments had attracted a little water and tested only 98·85 per cent. H_2SO_4: its action upon lead was 13½ times that of ordinary concentrated acid of 96·5

per cent. H_2SO_4. Fresh monohydrate of 99·5 or 99·75 per cent. would, no doubt, have shown even more action.]

10. *Nordhausen fuming oil of vitriol* acts upon lead much more strongly than ordinary concentrated acid. When it contains 20 per cent. free SO_3 it has 32 times the effect of ordinary acid; stronger Nordhausen acid has rather less effect than the 20 per cent. acid, because a protective coat of lead sulphate is formed. At all events lead must not be brought into contact with Nordhausen acid.

11. *Nitric acid* of sp. gr. 1·37 to 1·42 may be brought into contact with lead *at the ordinary temperature*, but no acid of less strength. Stronger acid than the above acts more powerfully upon lead, but no more than concentrated sulphuric acid. *Mixtures of concentrated sulphuric acid and strong nitric acid* act very little indeed upon lead, much less than either strong sulphuric acid or strong nitric acid by themselves; such mixtures can be treated in lead vessels without any hesitation. (Later observations have shown that this applies only to *ordinary temperatures* and when no moisture can be attracted from the air. *Hot* mixed acids act strongly on lead.)

12. Mixtures of *sulphuric acid and nitroso-sulphuric acid*, partly also containing *nitric acid*, all of them originally containing 0·1 per cent. N, but by heating to 65° C., brought to the state in which they can really exist in vitriol-chambers, give the following results:—If a little nitric acid is added to dilute sulphuric acid, and the mixture is heated, a little HNO_3 is volatilised, but no nitrosyl-sulphuric acid is formed until the concentration has reached sp. gr. 1·5. From this point oxygen escapes, and at sp. gr. 1·768 the whole of the HNO_3 has vanished, SO_5NH appearing in its stead. Inversely, nitric acid is formed from nitrous sulphuric acid on diluting it; in the case of prolonged heating, this evidently takes place not by splitting up into HNO_2 and NO, but by absorption of oxygen from the air.

The action of the acid on lead is least just about the lowest point where the nitrosyl-sulphuric acid is still capable of existing. It increases with its dilution, and in proportion to this, evidently through the formation of nitric acid, equally with its concentration, and later on rapidly so, the action of stronger sulphuric acid combining with that of nitrosyl-sulphuric acid and nitric acid. *The minimum action is between sp. gr.* 1·5 *and* 1·6—*that is, just at that concentration above or below which the acid ought not to be kept in vitriol-chambers.* This proves that it is not rational to keep the acid in the first chamber too strong (*cf.* Chapter VII.).

Bismuth is generally (as shown above) considered very injurious to the resisting-quality of lead for sulphuric acid. H. O. Hofmann (*Min. Ind.*, v. p. 398) certainly states that bismuth up to 2 per cent., or up to the amount usually found in commercial lead, does not affect its resistance in vitriol-chambers, and that it is far more important that the surface should be clean and smooth, to prevent droplets of condensed acid adhering to the lead. While the second part must be accepted without contradiction, the first (concerning the bismuth) is contrary to every other experience. In a special case which has come under my notice, two Glover towers behaved quite differently, one of them going without lead repairs for thirteen years, the other one being damaged before two years were over. Analysis proved the lead to be of almost identical composition in both cases; but the first contained 0·004, the second 0·012 per cent. bismuth.

According to Junge (*Sachs. Jahresber. f. Berg- u. Hüttenwesen*, 1895) some acid-makers prefer lead desilverised by the Pattinson process to that treated by the Parkes process, because the latter is supposed to contain more zinc; but Hofmann proves this to be contrary to facts; Parkes lead contains less zinc, but more bismuth, than Pattinson lead. It is not denied that in concentrating-pans Pattinson lead stands better than Parkes lead. This would be explained by the fact that Pattinson lead contains more copper and less bismuth than Parkes lead (cf. *suprà*, p. 326)

Fluorides sometimes occur in blende, and they may cause trouble, as they are converted into HF in the Glover tower, and this acid contaminates the sulphuric acid. Prost (*Chem. Zeit.*, 1902, p. 12) asserts that even a very slight quantity of HF in sulphuric acid causes great wear and tear of the lead of Glover towers and chambers, not only directly, but by facilitating the corrosion by sulphuric acid and the nitrogen acids. Most descriptions of blende contain only traces of fluorine, but once he found 7 per cent. (The experiments quoted in the original do not show any essential difference between pure acids and those containing up to 2 per cent. HF in their action on lead. Gaseous HF seems to act much more than that contained in sulphuric acid.)

About the behaviour of *zinc* towards sulphuric acid, I will only quote the fact that concentrated acid yields hydrogen, together with hydrogen sulphide, down to acid of the formula $SO_4H_2, 5H_2O$. Acid of the formula $SO_4H_2, 6H_2O$ yields pure hydrogen (Muir and Robb, *Chem. News*, xlv. p. 70).

Hart (*J. Soc. Chem. Ind.*, 1907, p. 668) found the formation of easily fusible alloys of lead with aluminium, tin or zinc to be the most frequent cause of the leaking of lead pans; bismuth has a similar but slower action; antimony acts as well injuriously, but copper, arsenic, and silver very little, and copper, under certain circumstances, may even act as a protective agent. The physical condition of the lead is also of importance.

Tin is not acted upon by acid of the formula $SO_4H_2, 3H_2O$.

Behaviour of Sulphurous and Sulphuric Acid towards the Oxides of Nitrogen.

The reactions between the oxides and acids of sulphur and nitrogen are of extreme importance for the theory of the sulphuric-acid process in general, and for the recovery of the nitrogen compounds in particular.

The older researches in this field, of Clément-Desormes, Dalton, Davy, Berzelius, Gay-Lussac, W. Henry, Gaultier de Claubry, De la Provostaye, A. Rose, Koene, Weltzien, Rebling, and Muller, have now merely an historical interest. The modern literature of this subject begins with the labours of R. Weber, during the years 1862 to 1867, published in the *J. prakt. Chem.*, lxxxv. p. 423, and c. p. 37; Poggendorff's *Annalen*, cxxiii. p 341, cxxvii. p. 543, cxxx. p. 277; and partly in *Dingl. polyt. J.*, clxvii. p. 453. Other very important papers have been published by Cl. A. Winkler ("Researches on the Chemical Processes going on in the Gay-Lussac Towers," Freiberg, 1867), by Rammelsberg (*Ber.*, 1872, p. 310), by Michaelis and Schumann (*ibid.*, 1874, p. 1075).

My own researches referring to this subject are found in the following publications:—1877: *Berl. Ber.*, x. pp. 1073 and 1432. 1878: *Berl. Ber.*, xi. pp. 434 and 1229; *Dingl. polyt. J.*, ccxxviii.

pp. 70, 548, and 553. 1879: *Dingl. polyt. J.*, ccxxxiii p. 63; *Berl. Ber.*, xii. pp. 357 and 1058. 1881: *Berl. Ber.*, xiv pp. 2188 and 2196. 1882: *Berl. Ber.*, xv. pp. 488 and 495. 1884: *Chem. Ind.*, 1884, p. 5. 1885: *J. Soc. Chem. Ind.*, pp. 31 and 447; *Berl. Ber.*, xviii. pp. 1376, 1384, 1391; *J. Chem. Soc.*, xlvii. pp. 457 and 465. 1888: *Berl. Ber.*, xxi. pp. 67 and 3223. 1889: *Z. angew. Chem.*, pp. 265 and 385. 1890: *ibid.*, p. 195. 1899: *ibid.*, p. 393.

Of the different oxides of nitrogen, *nitrous oxide*, N_2O, need not detain us here. It is very slightly soluble in sulphuric acid, much less so than in pure water, as, once formed, it is not oxidised again into NO or higher nitrogen oxides; it is altogether lost for the manufacture of sulphuric acid, nor does it form any chemical compound with that acid.

Nitric oxide, NO, was stated by Henry and Plisson to be absorbed by oil of vitriol, if left a long time in contact with it, with formation of nitrous pyrosulphuric anhydride (see below); but Berzelius, Gay-Lussac, and many others have long ago refuted this statement, more especially Winkler (*loc. cit.*, p. 58). In fact the sulphuric acid of the absorbing-apparatus cannot retain that portion of the nitrogen oxides which have been reduced to the state of nitric oxide; and from this follows the necessity of an excess of oxygen in the gas issuing from the chambers, since only this prevents the existence of nitric oxide in the same. Small quantities of nitric oxide may, however, escape oxidation even in the presence of oxygen, and are hence found in the chamber exit-gases.

The solubility of NO in sulphuric acid, although not *nil*, is extremely slight. Cl. Winkler already in 1867 showed that it is not absorbed by strong vitriol. Kolb also made experiments with acids of varying concentration (*Bull. Soc. Ind. Mulhouse*, 1872, p. 225), and found that acid of 1·841 does not absorb even traces of NO; acid of 1·749 to 1·621 merely traces (2 to 6 mg. to 100 g. acid); acid of 1·426 absorbs 0·017 g. NO; acid of 1·327, 0·020 g. NO to 100 g. My own experiments (*J. Soc. Chem. Ind.*, 1885, p. 447, and 1886, p. 82; also *Berl. Ber.*, 1885, p. 1391, and 1886, p. 111), show that concentrated O.V. absorbs per cubic centimetre only 0·0000593 g. = 0·035 c.c. NO, and acid of sp. gr. 1·500 only half that quantity.

In the presence of oxygen nitric oxide is absorbed by sulphuric acid (Bussy, Winkler); but then it is really nitrous acid which is absorbed; and Winkler was the first to prove that it is precisely the presence of sulphuric acid which causes the oxidation not to proceed beyond the formation of nitrous acid, the latter combining afterwards with the sulphuric acid to form nitroso-sulphuric acid and water:—

$$2SO_2(OH)_2 + N_2O_3 = 2SO_2(OH)(ONO) + H_2O.$$

In several of the above-quoted papers I have given clear proofs of the same fact, viz., that on passing nitric oxide, together with a very large excess of free oxygen, through strong sulphuric acid, nothing but nitroso-sulphuric acid is formed, which means that 2NO take up only 1 O; but once out of the range of the acid, immediately above it, the reaction $2NO + O_2 = N_2O_4$ sets in, and this compound, when afterwards meeting sulphuric acid, yields equal molecules of nitric acid and of nitroso-sulphuric acid (*vide infrà*).

Nitrous Acid.—Real nitrous acid, HNO_2, is not known in the pure state, only in that of dilute solutions. When dissolving nitrous anhydride, N_2O_3, in water, some nitrous acid is formed and remains dissolved in the excess of water, but much of it splits up according to the formula:—

$$3NO_2H = 2NO + NO_3H + H_2O.$$

The anhydride, N_2O_3, also called nitrogen trioxide, is known as a dark blue liquid which boils below 0° C. Wittorf (*Z. anorg. Chem.*, xli. 85) has obtained N_2O_3 in the crystallised state. The vapours immediately dissociate for the most part into NO and NO_2 (with more or less N_2O_4, according to temperature), but a small quantity of N_2O_3 evidently exists even in the state of vapour. We shall not here enter upon the much debated question concerning the existence of N_2O_3 in the gaseous state, but merely quote the literature: Luck (*Berl. Ber.*, 1878, pp. 1232 and 1643), Witt (*ibid.*, p. 2188), Ramsay and Cundall (*J. Chem. Soc.*, xlvii. pp. 187, 672), Lunge (*ibid.*, p. 457; *Z. anorg. Chem.*, vii. p. 209), Dixon and Peterkin (*Proc. Chem. Soc.*, May 1899, p. 115). H. Brereton Baker and Muriel Baker (*Trans. Chem. Soc.*, 1907, xci. p. 1862) have shown that in the dried condition gaseous N_2O_3 can be most certainly obtained.

Although there is no doubt about the fact that most of the "nitrous vapours," formerly considered as N_2O_3 in the state of gas or vapour, is in reality principally a mixture of nitrogen oxide (NO) and peroxide (which, for the sake of simplicity, we shall in this case consider as NO_2), with very little N_2O_3, we must bear in mind the equally undoubted fact that a mixture of equal molecules of NO and NO_2 behaves in all its reactions towards other chemical compounds exactly as if it were N_2O_3. When passed into an alkaline solution, it quantitatively yields a nitrite:

$$2NaOH + NO + NO_2 = 2NaNO_2 + H_2O.$$

When brought into contact with concentrated sulphuric acid it is quantitatively converted into nitroso-sulphuric acid:

$$2H_2SO_4 + NO + NO_2 = 2SO_5NH + H_2O.$$

We have, therefore, the right to assume that such a mixture of equal molecules of NO and NO_2 *chemically* comes to the same thing as gaseous N_2O_3; and we shall throughout this book simplify many of our explanations and discussions by speaking of the above mixture as N_2O_3, although *physically* it is only a mixture of NO and NO_2. We are all the more entitled to do this, since there is no doubt that *some* N_2O_3 exists in the gaseous state as such, and since, according to the law of mass action, this N_2O_3 must be constantly reformed when taken away by some chemical reaction.

I have all the more right to take this line, since everybody speaks of distilling sulphuric acid or subliming ammonium chloride, although we know that on distillation nearly all sulphuric acid is split up into SO_3 and H_2O, which recombine on condensation (*cf.* p. 287), and ammonium chloride in the state of vapour is mostly $= NH_3 + HCl$.

Nitrous anhydride (*nitrogen trioxide*), N_2O_3, dissolves in sulphuric acid, all the more easily when the latter is concentrated, but also, as we shall see, when it contains a certain amount of water. The reaction taking place is this:

$$2H_2SO_4 + N_2O_3 = 2SO_5NH + H_2O.$$

Rammelsberg (*loc. cit.*) asserts that when nitrous anhydride is employed in excess, nitric acid and nitric oxide are also formed:

$$H_2SO_4 + 2N_2O_3 = SO_5NH + HNO_3 + 2NO;$$

but this reaction only takes place in presence of water, and the formation of nitric acid and nitric oxide must be regarded as a secondary reaction, owing to the well-known action of free nitrous acid on an excess of water. Where there is enough sulphuric acid and no excess of water, Rammelsberg's reaction does not come into play.

The compound formed by the action of nitrous acid on sulphuric acid possessing the empirical formula SO_5NH, has long been known, both in the solid state, as "chamber-crystals," and dissolved in an excess of sulphuric acid, as "nitrous-vitriol"; but its true composition as *nitroso-sulphuric acid* has only comparatively recently been elucidated.

The easiest way of preparing the *chamber-crystals* in a state of purity is by conducting sulphur dioxide into well-cooled fuming nitric acid until the whole mass has been converted into a magma, but not until the nitric acid has been entirely decomposed, and drying the crystallised mass on a porous slab under a bell-jar over some oil of vitriol. Obtained in this way, or collected in the connecting-pipes of vitriol-chambers or other places where there is a deficiency of steam, they consist of four-sided prisms or orthorhombic crystals; but generally, when prepared on the small scale, they appear as a scaly, feather-like, or granular mass, colourless and transparent. Their fusing-point is stated by Weltzien = 73°, by Gaultier de Claubry = 120° to 130°; but they are partly decomposed before fusing, with evolution of red fumes.

The composition of chamber-crystals was formerly uncertain; the question was, in the language of the older chemists, whether they were a compound of sulphuric acid with nitrogen peroxide or with nitrous acid (nitrogen trioxide). Müller (*Ann. Chim. anal.*, cxxii. p. 1) still pronounced for the former; but R. Weber proved in 1862, and more rigorously in the following year, by estimating all their constituents according to unexceptionable methods, that their formula must be constructed on the second supposition. His results were as follows:—

	Molecular weight.	Calculated	Found.	
$2\ SO_3$ . .	160	62·39	64·00	63·90
N_2O_3 . .	76	29·92	27·96	27·14
H_2O . .	18	7·79	10·50	9·50
SO_3, N_2O_3, H_2O .	254	100·00	102·46	100·54

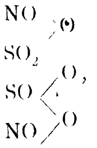
This formula has also been confirmed by Michaelis and Schumann (*Ber.*, 1874, p. 1075), who at the same time maintained, from the products of the decomposition of chamber-crystals by phosphorus perchloride, that the compound whose molecular weight has to be halved must be regarded as *nitrosulphonic acid*, $SO_2\langle\begin{matrix}OH\\NO_2\end{matrix}$—that is, as sulphuric acid, one of whose hydroxyls is replaced by the nitro group, or as nitric acid, for whose hydroxyl is substituted the sulpho group. This mode of explaining the constitution of that substance cannot, however, be strictly maintained. Both from its formation and the decomposition, it is certain that it does not contain the nitro group NO_2, but the nitroso group NO. Its formula must therefore be written:

$$SO_2\begin{matrix}—OH\\—ONO\end{matrix}, \text{ or } SO_2(OH)\,(ONO),$$

and it must be called nitrosyl sulphate, or nitrosyl-sulphuric acid, or nitroso-sulphuric acid, which means sulphuric acid, one of whose hydrogen atoms is replaced by the nitroso group, that is the radical of nitrous acid, NO(OH). It is a mixed anhydride of sulphuric and nitrous acid, as is proved both by its formation and its decomposition by water.

Jurisch gives to the chamber-crystals ("Weber's acid") the formula · H_2O, O_3S, SO_3, O_3N_2.

There exists also a complete anhydride of nitroso-sulphuric acid, of the empirical formula, N_2O_3, $2SO_3$, which is rationally written:



$$\begin{matrix}NO\\SO_2\\SO\\NO\end{matrix}\begin{matrix}\rangle O\\ \\ \langle\begin{matrix}O,\\O\end{matrix}\end{matrix}$$

but this is only formed by mixing liquid sulphur dioxide and nitrogen tetroxide in the cold under pressure (Provostaye), or sulphuric anhydride with dry nitric oxide (H. Rose), or by heating sulphuric anhydride with nitrogen tetroxide (Weber), none of which reactions are possible in the manufacture of sulphuric acid.

Neither is this the case with the compound produced by R. Weber (*Poggend Annalen*, clxii. p. 602) by conducting sulphuric anhydride into the most highly concentrated nitric acid, which has the empirical formula N_2O_5, $4SO_3$, $3H_2O$.

Nitroso-sulphuric acid is formed not merely as above indicated, but in many other ways. We have already mentioned its formation from sulphur dioxide and nitric acid:

$$SO_2 + NO_3H = SO_2(OH)(ONO).$$

It is also formed when a mixture of strong sulphuric and nitric acids is heated, oxygen being evolved (A. Rose, and later on Lunge, *cf.* p. 343):

$$H_2SO_4 + HNO_3 = SO_2(OH)(ONO) + H_2O + O.$$

On the other hand, sulphur dioxide can form that compound even with the lower oxides of nitrogen, if there is water and (except with N_2O_4, where this is unnecessary) oxygen present. In the perfectly dry state sulphur dioxide does not act on the dry nitrogen oxides; but in presence of the smallest quantity of water "chamber-crystals" are formed, if SO_2 meets with N_2O_4, or with NO or N_2O_3 and oxygen. Winkler has shown that, in an atmosphere of moist carbon dioxide, nitrogen trioxide does not form chamber-crystals with sulphur dioxide, but nitrogen peroxide does so, and he distinguishes N_2O_3 and N_2O_4 in this manner. The fumes of N_2O_3, with an excess of SO_2 and H_2O, but in the absence of oxygen, give no chamber-crystals at all; they are decolorised, nitric oxide and sulphuric acid being formed. If oxygen or air is admitted, chamber-crystals instantly appear, and this is also the case when nitrogen peroxide meets sulphurous acid in the presence of water. These observations of Winkler's have been repeatedly confirmed; but we must now add that what he called "fumes of N_2O_3" is in reality mostly a mixture of equal molecules of NO and NO_2, behaving *chemically* like N_2O_3.

As some points had not been entirely cleared up by previous investigators, and there were partial contradictions among their results, I undertook a new investigation on the *interaction of sulphur dioxide and nitric oxide, with or without the presence of water* (*Berl. Ber.*, xiv. pp. 2196 *et seq.*), which led to the following results:—

1. Dry NO and SO_2 have no action upon one another, be it at the ordinary temperature, or at 50° or at 100°, provided that air and moisture are rigorously excluded.

2. NO, SO_2, and water act in such a way that as much N_2O is formed as corresponds to the quantity of SO_2 originally present. A reduction down to N could not be established.

3. If NO and SO_2 meet in the presence of dilute sulphuric acid, of sp. gr. 1·455, no reduction of NO to N_2O takes place, even when there is a very large excess of SO_2 present, whether the digestion be carried on for many hours at ordinary temperature or at 60°. Even with acid of sp. gr. 1·32 no reduction of NO by SO_2 could be established.

4. If NO, SO_2, and oxygen meet in the presence of water, a slight but distinct reduction down to N_2O takes place. If, however, in lieu of water, dilute acid of sp. gr. 1·32 is employed, no such reduction can be observed.

The bearing of these results on the theory of the chamber-process will be discussed later on (Chapter VII.).

A further investigation by myself (*Berl. Ber.*, xviii. p. 1384; *J. Chem. Soc.*, xlvii. p. 465) confirmed the above results. It was shown that in the dry state nitric oxide combines with an excess of oxygen to form N_2O_4 exclusively, or nearly so; dry nitric oxide in excess with oxygen yields N_2O_3 along with N_2O_4; in the presence of water, NO with an excess of oxygen is altogether converted into nitric acid. If, however, NO meets O in immediate contact with concentrated sulphuric acid, there is no formation of either N_2O_4 or HNO_3, even with the greatest excess of oxygen; oxidation proceeds only to the stage of N_2O_3, which, however, is not formed in the free state, but is at once converted into nitroso-sulphuric acid:

$$2SO_4H_2 + 2NO + O = 2SO_2(OH)(ONO) + H_2O.$$

Outside the immediate contact with the acid the reaction is again as before with dry gases, viz. $2NO + O_2 = N_2O_4$; that is, here NO is oxidised to a higher state than within the sulphuric acid.

A very elaborate investigation of the interaction between nitrous and sulphurous acid was published by Raschig (*Lieb. Ann.*, ccxli. pp. 161 *et seq.*). He found a number of new compounds, and rectified some of the statements of Frémy and Claus concerning compounds formerly described by them. He also discovered a very convenient method of preparing hydroxylamine. But as nearly all Raschig's experiments were made with alkaline solutions, and those which were performed with acid solutions were made under conditions utterly different from those of a lead chamber, namely at the freezing-point, we cannot stop to give any details of his results. Under the just-mentioned circumstances, apart from N_2O and NO, amidosulphonic acid, hydroxylamine, and ammonia are observed, but only in small quantities; and above the low temperatures employed by Raschig the occurrence of those substances is altogether too uncertain and minimal to be taken into consideration for our purposes.

Action of water on chamber-crystals.—These crystals are very deliquescent; they absorb water rapidly from ordinary air. In contact with a little more water, they dissolve quickly with evolution of heat, much nitric oxide being given off. When introduced into a large quantity of water, they dissolve without visible evolution of gas; but in point of fact nitric oxide is formed as well, also nitric acid, together with nitrous acid. This has led to many attempts at explanations, and Rammelsberg and Philipp have asserted that exactly $\frac{1}{4}$ of the nitrogen appears as NO, $\frac{5}{8}$ as nitrous acid, and $\frac{1}{8}$ as nitric acid:

$$16SO_2(OH)(ONO) + 9H_2O = 16SO_4H_2 + 4NO \\ + 2NO_2(OH) + 5N_2O_3.$$

But this complicated and very unlikely reaction need not be assumed at all. Every fact observed in this connection can be quite simply explained by the following reaction:

$$SO_2(OH)(ONO) + H_2O = SO_4H_2 + NO(OH);$$

that is, nitroso-sulphuric acid takes up the elements of water, to form sulphuric acid and nitrous acid; the latter, as is well known, is unstable in the presence of an excess of water, and hence partly splits up into nitric oxide and nitric acid:

$$3NO_2H = NO_3H + 2NO + H_2O.$$

In the presence of less water, nitrous anhydride can be formed from chamber-crystals, and escapes in the shape of brown fumes (of course mostly dissociated into nitric oxide and peroxide):

$$2SO_2(OH)(ONO) + H_2O = 2SO_4H_2 + N_2O_3.$$

For nearly every purpose nitroso-sulphuric acid or its solution in sulphuric acid may be regarded as a solution of nitrous acid in sulphuric acid.

The behaviour of nitroso-sulphuric acid towards sulphuric acid of various concentrations is of great interest for our purposes. In concentrated oil of vitriol the crystals dissolve easily and without decomposition. This solution is stable enough to be distilled without losing any nitrous acid, whilst the isolated crystals are decomposed on being gently heated. I have shown (*Z. angew. Chem.*, 1888, p. 661, and 1890, p. 447) that on distilling such a solution for four hours, when 40 per cent. of the sulphuric acid had passed over, the distillate contained only 5 per cent., the residue 95 per cent. of the nitrous acid, none of it having been destroyed. It is possible to obtain solutions of 1·9 sp. gr.; they evolve with water nitric oxide, inflame phosphorus at 62° C., oxidise sulphur and many metals on distillation with evolution of NO; heated with ammonium sulphate to 160° they evolve nitrogen gas. Sulphur dioxide evolves nitric oxide; but a solution of nitroso-sulphuric acid in strong oil of vitriol (of 170° Tw.), even on long-continued treatment with dry sulphur dioxide, is only incompletely decomposed, and on addition of water still shows the presence of nitrous acid by the evolution of brown vapours. This explains the fact (well known to manufacturers) that *concentrated* sulphuric acid contaminated by nitrous acid is only with difficulty purified by sulphur dioxide. At a higher temperature sulphur dioxide decomposes chamber-crystals with evolution of nitrous oxide (Frémy). Further statements respecting the behaviour of sulphur dioxide towards the solution of chamber-crystals in sulphuric acid, the so-called "nitrous vitriol," will be made when examining the process going on within the Glover tower. It is remarkable, and of great importance for the practice of sulphuric-acid making, that even dilute acids of 1·70 down to 1·55 sp. gr. dissolve the crystals in the cold without decomposition; the decomposition only commences when the specific gravity of the dilute acid has fallen below 1·55 —that is, below the density of ordinary chamber acid.

Nitrogen peroxide,[1] whether in the state of a liquid or a gas, strongly acts on sulphuric acid. If, according to Weber, nitrogen peroxide, made by gently heating fuming nitric acid [and therefore not quite free from nitric acid], be added to sulphuric acid of different degrees of concentration, the following is observed:—The strongest oil of vitriol, down to 1·7 sp. gr., absorbs the nitrogen peroxide without coloration. Acid of 1·55 turns yellow; here the nitrogen peroxide is probably absorbed to a large extent similarly as by nitric acid, and no decomposition, as represented by the equation on p. 341, has taken place, while this has to be assumed in the case of the stronger acids. Acid of 1·49 turns greenish-yellow; of 1·41 intensely green; acid of 1·31 turns blue and evolves nitric oxide, which on applying a gentle heat escapes with violent effervescence. Weak acids are only coloured for a short time. From this Weber inferred:—that acids of 1·8 to 1·7 combine with nitrogen peroxide with formation of nitroso-sulphuric acid; weaker acids simply absorb it; and the more dilute acids decompose it with formation of nitric oxide, nitrous acid, and nitric acid. The action of sulphurous acid on these mixtures is different according to their concentration. As mentioned above, the solution of chamber-crystals in concentrated sulphuric acid is but incompletely decomposed even by a prolonged action of sulphurous acid; but the yellow mixture of 1·55 sp. gr. and the coloured, more dilute, acids are decomposed with strong effervescence of nitric oxide. It will be shown afterwards what part all these reactions play in the recovery of the nitrous gas in the manufacture, where the object is first to absorb the gas in sulphuric acid of 1·7, and then again to liberate it from that solution.

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[1] We shall generally give this name to the compound formerly called "hyponitric acid" and now sometimes "nitrogen tetroxide" or "nitrogen dioxide." It is generally assumed that in the gaseous state it consists of a mixture of molecules of NO_2 and N_2O_4, of varying proportions, according to

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the temperature. At a low temperature, especially in the liquid state, it is $= N_2O_4$; above 140° $= NO_2$. The following are the intermediate proportions:—

	C	Per cent. N_2O_4	Per cent. NO_2.
At	26·7	80	20
„	39·8	71	29
„	60·2	47	53
„	80·6	23	77
„	135	1	99

The formula N_2O_4 was again maintained by Piloty and Schwerin (*Ber.*, 1901, pp. 1887 and 2354), but Divers (*Proc. Chem. Soc.*, xix. p. 283) declares the true formula to be NO_2, viz., O : N·O, that is trivalent nitrogen combined with an ordinary bivalent and with a *univalent* oxygen atom.

Winkler gave a different account of the behaviour of liquid nitrogen peroxide from that of Weber. He stated that it may be mixed with sulphuric acids down to 142° Tw., but that it yields a solution totally different from that of chamber-crystals in sulphuric acid, viz., a liquid of yellow colour and constantly evolving red fumes. On heating, it effervesces and gives off streams of gaseous nitrogen peroxide; if the mixture is made with sulphuric acid of 142° Tw., the NO_2 completely volatilises far below the boiling-point of sulphuric acid, so that the residue on dilution with water does not decolorise potassium permanganate. If, however, acid of 170° Tw. has been employed, the liquid on heating certainly yields up the larger portion of its NO_2; but the residue behaves like a solution of chamber-crystals in sulphuric acid, and on being mixed with water it evolves red fumes which can be proved to be N_2O_3, not NO_2, by their not forming any chamber-crystals with moist SO_2.

There are some essential differences between the statements of Weber and those of Winkler, more especially so far as the behaviour of nitrogen peroxide is concerned, which were cleared up by my own researches (see below).

If concentrated sulphuric acid is mixed with a little concentrated *nitric acid*, and sulphur dioxide is passed into the mixture, the nitric acid in the cold is only reduced to nitrous acid, which remains combined with the sulphuric acid: this compound resists the further action of the sulphur dioxide in the same way as the solution prepared from concentrated oil of vitriol and chamber-crystals. On the other hand, more dilute mixtures of sulphuric and nitric acid, below 1·7 sp. gr., are more or less easily decomposed by SO_2, in the ratio of their dilution.

Since the labours of Weber and Winkler did not in all points agree with one another, and the subject seemed to call for another investigation, I undertook a long research (*Dingl. polyt. J.*, ccxxxiii. p. 63), the conclusions of which (also published in the *Berl. Ber.*, xii. p. 1058) are as follows:—

1. Nitrogen peroxide, under ordinary circumstances, cannot exist in contact with sulphuric acid, but at once splits up into nitrous acid, which, with a portion of the sulphuric acid, yields nitroso-sulphuric acid and nitric acid (dissolving as such) thus:—

$$N_2O_4 + SO_2(OH)_2 = SO_2(OH)(ONO) + NO_3H.$$

2. Nitroso-sulphuric acid, on dissolving in an excess of sulphuric acid, forms a colourless liquid, but only up to a certain limit of saturation, which is all the higher the more concentrated the sulphuric acid. This limit for acid of sp. gr. 1·84 is not yet reached at 55·34 mg. N_2O_3 = 185 mg. $SO_2(OH)(ONO)$ in 1 c.c. of acid.

3. Beyond that limit at first a yellowish tint appears, of course with stronger acids only when more nitroso-sulphuric acid is present than with weaker acids. This took place with a mixture of sp. gr. 1·887 (made from pure sulphuric acid of sp. gr. 1·84), containing in 1 c.c. 147 mg. N_2O_3 = 372 mg. $SO_2(OH)(ONO)$, and also with acid of sp. gr. 1·706, containing in 1 c.c. only 56·7 mg. N_2O_3 = 190 mg $SO_2(OH)(ONO)$. Since these acids also are rendered colourless by prolonged boiling, the excess of nitroso-sulphuric acid seems to be rather loosely held; but the temperature of the water-bath is not sufficient to affect it.

4. The phenomenon observed by Winkler, a mixture of strong vitriol and nitrogen peroxide showing an orange-colour even when cold, emitting red vapours, and exhibiting a tempestuous evolution of nitrogen peroxide on being gently heated (which proves the existence of unchanged nitrogen peroxide), can evidently take place only when the mixture contains *far* more N_2O_4 than the strongest mentioned above, or the strongest ever occurring in sulphuric-acid works under any circumstances. Many experiments of heating in the water-bath for a prolonged period demonstrate the absence of free N_2O_4 in all cases observed. Still less can the presence of nitrogen peroxide be assumed in more dilute acids; it is therefore inadmissible to cite it as such in analyses.

5. All nitrous vitriols, *i.e.*, solutions of nitroso-sulphuric acid in sulphuric acid, whether they contain nitric acid at the same time or not, on being heated far below their boiling-point assume a golden-yellow or even darker yellow colour, but entirely lose it again on cooling. This change of colours may be repeated any number of times. It hardly indicates a loosening of the combination, since this proves to be very stable even at much higher temperatures; but it may rather be compared to the deeper colour which ferric-chloride solutions assume on being heated.

6. The stability of nitroso-sulphuric acid in its solution in sulphuric acid is very great, even at the boiling-point, providing the sp. gr. is not below 1·70. It is true that on boiling it some nitrogen is always lost, and all the more the less concentrated the acid is; but if the boiling takes place so that the vapour cannot condense and flow back, there is some nitroso-sulphuric acid found in the residue, even from acid of sp. gr. 1·65 (*cf.* p. 339). But if the vapour is condensed and the condensing liquid (which, in the case of vitriol of sp. gr. 1·80 or below, consists of very dilute acid or almost pure water) is allowed to flow back, a considerable loss is caused by denitration.

7. Down to a concentration of sp. gr. 1·65 the affinity of sulphuric acid for nitrous acid, *i.e.*, the tendency to the formation of nitroso-sulphuric acid, is so great that any nitric acid present at the same time, whether added as such or formed by the decomposition of nitrogen peroxide, is reduced with loss of oxygen, and employed to form nitroso-sulphuric acid. In the case of acid of sp. gr. 1·71 and upwards, this transformation takes place almost completely after a brief boiling, but at sp. gr. 1·65 only incompletely. This is a further argument against the existence of N_2O_4 in the solution.

8. Below sp. gr. 1·65 the nitroso-sulphuric acid possesses so little stability that, for instance, from acid of sp. gr. 1·60 some nitrogen oxides (but only a very small percentage) are expelled in the water-bath, and nearly all of them by boiling for a short time. In the case of acid of sp. gr. 1·5, it is evident that, even without heating, the nitrous acid added is partly decomposed into nitric acid and nitric oxide; but after heating for an hour in the water-bath a considerable quantity of nitroso-sulphuric acid remains undecomposed, whilst another portion has been converted into sulphuric acid. In the case of still weaker acids, of course these phenomena occur even to a greater extent; but it is very probable that even very dilute sulphuric acid may contain, while cold, a little nitroso-sulphuric acid if reducing-agents are absent.

9. Most of the nitric acid present together with nitroso-sulphuric acid in dilute acids (of sp. gr. 1·5 and below) remains behind in the liquid even after prolonged boiling. If, therefore, the nitrous vitriol of acid-works, in consequence of a faulty process, contains nitric together with nitrous acid, it cannot

possibly be completely denitrated by hot water or steam, in which case a lower strength than sp. gr. 1·5 is never reached; the denitration can only be effected by reducing-agents, such as sulphur dioxide in the Glover tower or mercury in the nitrometer. In the latter it can be very clearly seen with how much more difficulty and slowness the denitration goes on in the presence of nitric acid.

10. The tendency to form nitroso-sulphuric acid is so strong that even on passing a large quantity of air (oxygen) through sulphuric acid together with nitrous acid, no oxidation of N_2O_4 or N_2O_5 takes place, just as in the case of oxygen and NO.

11. Nitrous acid cannot be absorbed by caustic-soda solution without loss, because a portion of it is decomposed into nitric acid and nitric oxide.

12. The purple colour which is developed in nitrous vitriol by the action of reducing-agents is caused by a solution of nitric oxide in such acids, and is possibly produced by a very unstable compound of nitrogen and oxygen, midway between NO and N_2O_3.

Although my experiments had decidedly proved (*cf.* Nos. 1 and 4 of the just-quoted conclusions) that nitrogen peroxide does not dissolve as such in sulphuric acid, with formation of an unstable solution from which the N_2O_4 can be drawn off by heating, the former erroneous assertion of Winkler (since that time recognised as such by himself) did not vanish from chemical literature, and, for instance, gave rise to a decidedly erroneous explanation of the process of Lasne and Benker for carrying on the work in the Gay-Lussac tower. This caused me to investigate the subject once more (*Berl. Ber.*, xv. p. 488). I pointed out that mixtures of pure nitrogen peroxide with even somewhat dilute sulphuric acid, down to sp. gr. 1·65, behave quantitatively like mixed solutions of equal molecules of nitroso-sulphuric acid and nitric acids; that on prolonged heating in a water-bath such solutions in acid of sp. gr. 1·75 do not lose any, and in acid of sp. gr. 1·65 only very little, of their nitrogen compounds. On prolonged boiling part of the latter escapes, but a large quantity of nitroso-sulphuric acid remains behind, more than that originally present, part of the nitric acid having passed into it with loss of oxygen. The idea of a "loose" union between N_2O_4 and sulphuric acid must therefore be entirely abandoned; and from this follows the fallacy of the idea held by some manufacturers that N_2O_4 is less easily absorbed by sulphuric acid than N_2O_3, and that therefore much N_2O_4 is lost in the Gay-Lussac tower. I directly disproved this idea by showing that vapours of nitrogen peroxide are most easily, quickly, and completely absorbed by sulphuric acid of sp. gr. 1·71, such as is used in the Gay-Lussac tower, and that this (colourless) solution is not changed either by long heating to 100° or by passing a current of air for a long time through it.

A concluding investigation on the behaviour of nitrogen peroxide towards sulphuric acid has been made by myself together with Weintraub (*Z. angew. Chem.*, 1899, p. 393), of which I here give merely a summary of the results.

1. The reaction between sulphuric acid and nitrogen peroxide is reversible, since the nitric acid formed has some action on nitroso-sulphuric acid, forming sulphuric acid and nitrogen peroxide:

$$H_2SO_4 + N_2O_4 \rightleftarrows SO_5NH + HNO_3.$$

In mixtures of sulphuric acid and nitrogen peroxide an equilibrium is formed, all four substances—sulphuric acid, nitrogen peroxide, nitroso-sulphuric acid, and nitric acid—being present at the same time. 2. In contact with concentrated sulphuric acid (95 per cent. H_2SO_4) nearly all the nitrogen peroxide is converted into nitroso-sulphuric and nitric acid. The inverse reaction sets in to a sensible extent only when very little sulphuric acid is present in comparison with nitric acid. 3. The affinity of sulphuric acid for nitrogen peroxide quickly decreases with the increase of water, so that in the case of sulphuric acid of sp. gr. 1·65 the action of nitric acid on nitroso-sulphuric acid begins to prevail; therefore very much of the nitrogen peroxide added remains in the free state, although the quantity of HNO_3, which is only formed by the reaction itself, is but small. 4. In the practice of sulphuric acid manufacture, the quantity of sulphuric acid in the concentrated state so largely prevails over that of the nitric acid, that all nitrogen peroxide may be practically regarded as quantitatively changed into SO_5NH and HNO_3. This, of course, also holds good when absorbing nitrous gases in concentrated sulphuric acid for analytical purposes. Therefore the conclusions No. 1 and No. 4 (pp. 341 and 342), although not mathematically exact, are to all intents and purposes valid.

The tension of nitrous acid in presence of dilute sulphuric acid at different temperatures is a matter of great importance for the theory of the formation of sulphuric acid in the lead-chambers. The first observations on this point were published by Sorel (*Z. angew. Chem.*, 1889, p. 272); but these have become obsolete by the far more extended observations published by myself in *ibid.*, 1891, pp. 37 *et seq.* The following tables (Nos. 1, 2, 3, and 4, see pp. 347-350) constructed from these indicate the loss of N_2O_3 suffered by acids of four different concentrations, containing quantities of N_2O_3 varying from 1 g. per litre upwards, in a current of air at temperatures from 50° to 90° C.

The behaviour of nitroso-sulphuric acid towards reducing agents is of the greatest importance, both for the chamber-process in general and for the recovery of nitrogen compounds. The most important of the agents in question is *sulphur dioxide*, which acts as follows:—

$$2SO_2(OH)(ONO) + SO_2 + 2H_2O = 3SO_4H_2 + 2NO;$$

that is, it forms with nitroso-sulphuric acid both sulphuric acid and nitric oxide. This is the leading reaction of the Glover tower, as we shall see hereafter; and it must also occur within the chambers, more especially in the first part of the set.

Sorel (*Z. angew. Chem.*, 1889, p. 273) has shown that if a mixture of SO_2 and O is made to react upon nitrous sulphuric acid and NO, there may be either a reduction of nitrous acid to NO, or an oxidation of NO to N_2O_3 (in the shape of SO_5NH), according to variations in the following conditions: temperature, dilution of the acid, proportion between SO_2 and O, percentage of NO. The extreme cases were well known before: a reduction takes place at high temperatures, in case of scarcity of oxygen and excess of water; an oxidation in case of excess of oxygen, concentrated acid, and low temperatures. For the intermediate cases Sorel made some special experiments, from which it followed that in identical mixtures an increase of the temperature from 70° C. to 80° C. was sufficient to change the oxidation into reduction. At equal temperatures a reduction took place when the gaseous mixture contained 31 per cent.

1. *Nitrous Vitriol of Sp. Gr.* 1·720 (*say*, 78 *per cent.* H_2SO_4).

N_2O_3 originally present. Grammes in 1 litre.	Loss of N_2O_3 in grammes per litre at				
	50°	60°.	70	80°.	90 .
1	...		...	..	0·006
2	..	...	..		0·018
3	.	...	.	...	0·025
4	...		.	...	0·031
5		...		.	0·037
6		...			0·043
7	..	...	.	0·006	0·056
8			.	0·010	0·068
9		..		0·012	0·081
10	...	..	...	0·018	0·093
11	.			0·025	0·112
12		.	.	0·030	0·125
13	...		...	0·031	0·143
14				0·043	0·168
15			0·006	0·056	0·193
16		.	0·010	0·068	0·218
17	..	...	0·006	0·087	0·250
18	..	..	0·012	0·106	0·281
19	..	.	0·025	0·125	0·318
20	.	..	0·031	0·150	0·356
21	..	.	0·043	0·175	0·400
22	...	..	0·064	0·200	0·450
23	...	0·006	0·081	0·237	0·500
24	0·006	0·018	0·100	0·275	0·550
25	0·012	0·031	0·125	0·312	0·600
26	0·018	0·043	0·150	0·356	0·662
27	0·031	0·062	0·181	0·400	0·725
28	0·043	0·081	0·212	0·450	0·800
29	0·062	0·100	0·256	0·500	0·850
30	0·081	0·125	0·293	0·550	0·956
31	0·093	0·162	0·337	0·612	1·043
32	0·112	0·200	0·387	0·641	1·125
33	0·125	0·237	0·391	0·743	1·206
34	0·143	0·275	0·475	0·806	1·287
35	0·156	0·312	0·525	0·868	1·375
36	0·175	0·350	0·575	0·931	1·456
37	0·193	0·381	0·618	1·000	1·543
38	0·206	0·418	0·662	1·062	1·625
39	0·237	0·456	0·718	1·125	1·712
40	0·268	0·500	0·775	1·193	1·800
41	0·293	0·543	0·831	1·256	1·890
42	0·325	0·587	0·887	1·331	1·975
43	0·350	0·631	0·937	1·400	2·062
44	0·376	0·675	0·993	1·468	2·150
45	0·406	0·712	1·050	1·537	2·237
46	0·437	0·756	1·106	1·606	2·325
47	0·462	0·800	1·162	1·675	2·392
48	0·493	0·837	1·218	1·743	2·500
49	0·518	0·881	1·268	1·806	2·587
50	0·550	0·921	1·325	1·875	2·675

2. *Acid of Sp. Gr.* 1·686 *(say, 76 per cent.* H_2SO_4*)*.

N_2O_3 originally present. Grammes in 1 litre.	Loss of N_2O_3 in grammes per litre at				
	50°.	60°.	70°.	80°.	90°.
8	...	...	.	...	0·025
9	...	...	.	...	0·036
10	...	...	...	0·012	0·050
11	...	...	...	0·018	0·062
12	...	...	...	0·025	0·086
13	...	...	0·010	0·050	0·125
14	.	...	0·012	0·075	0·162
15	...		0·025	0·100	0·225
16	...	..	0·050	0·150	0·286
17	...	0·010	0·062	0·200	0·350
18	...	0·012	0·100	0·262	0·436
19	...	0·025	0·150	0·350	0·525
20	...	0·050	0·186	0·425	0·625
21	...	0·075	0·250	0·525	0·750
22	...	0·112	0·300	0·650	0·975
23	..	0·136	0·350	0·775	1·200
24	...	0·175	0·400	0·900	1·436
25	0·010	0·200	0·462	1·025	1·662
26	0·012	0·236	0·512	1·175	1·900
27	0·025	0·262	0·562	1·300	2·125
28	0·036	0·300	0·612	1·436	2·350
29	0·050	0·336	0·675	1·575	2·600
30	0·062	0·362	0·750	1·700	2·812
31	0·100	0·412	0·850	1·812	3·086
32	0·136	0·462	0·950	1·975	3·350
33	0·186	0·512	1·050	2·100	3·625
34	0·225	0·575	1·150	2·236	3·900
35	0·275	0·625	1·250	2·362	4·175
36	0·312	0·675	1·336	2·500	4·450
37	0·350	0·725	1·436	2·625	4·736
38	c·400	0·525	1·536	2·762	5·000
39	0·436	0·836	1·636	2·900	5·275
40	0·486	0·886	1·736	3·025	5·550
41	0·550	0·950	1·850	3·150	5·850
42	0·612	1·050	1·986	3·275	6·125
43	0·686	1·125	2·112	3·412	6·400
44	0·750	1·212	2·250	3·525	6·700
45	0·825	1·300	2·325	3·736	6·975
46	0·886	1·3'6	2·500	3·825	7·250
47	0·962	1·475	2·636	3·962	7·536
48	1·025	1·512	2·762	4·100	7·825
49	1·100	1·650	2·886	4·236	8·100

SO_2, 10 per cent. O, 59 per cent. N, but an oxidation with a mixture of 21 SO_2, 12·1 O, 66·9 N, etc. The reaction of SO_2 on nitrous sulphuric acid is nothing like so simple as previously assumed. If the acid exceeds the strength of 1·630, the SO_2 does not reduce the N_2O_3 to NO, but forms with it and sulphuric

3. *Acid of Sp. Gr.* 1·633 (*say*, 71·5 *per cent.* H_2SO_4).

N_2O_3 originally present. Grammes in 1 litre.	Loss of N_2O_3 in grammes per litre at				
	50°.	60°.	70°	80°	90°.
1	0·012	0·025	0·036	0·100	0·150
2	0·050	0·075	0·086	0·225	0·300
3	0·100	0·150	0·186	0·350	0·436
4	0·162	0·212	0·300	0·536	0·612
5	0·212	0·300	0·436	0·736	0·825
6	0·300	0·425	0·636	1·000	1·112
7	0·400	0·562	0·836	1·275	1·425
8	0·500	0·712	1·036	1·550	1·750
9	0·600	0·835	1·236	1·812	2·062
10	0·700	0·936	1·436	2·086	2·375
11	0·800	1·125	1·636	2·350	2·712
12	0·871	1·262	1·825	2·636	3·075
13	0·986	1·400	2·036	2·900	3·436
14	1·086	1·536	2·225	3·175	3·800
15	1·186	1·675	2·412	3·450	4·162
16	1·275	1·800	2·612	3·725	4·512
17	1·375	1·936	2·786	4·000	4·886
18	1·475	2·036	2·975	4·262	5·236
19	1·562	2·250	3·186	4·550	5·600
20	1·662	2·412	3·400	4·850	5·986
21	1·812	2·612	3·650	5·162	6·400
22	1·975	2·812	3·912	5·512	6·862
23	2·186	3·062	4·250	5·912	7·425
24	2·436	3·336	4·612	6·350	8·036
25	2·700	3·636	5·000	6·800	8·662
26	3·000	3·950	5·412	7·300	9·362
27	3·312	4·300	5·850	7·812	10·150
28	3·662	4·636	6·325	8·400	11·000
29	4·025	5·012	6·812	8·025	11·986
30	4·412	5·412	7·350	9·675	13·125
31	4·800	5·836	7·950	10·386	14·500
32	5·236	6·325	8·575	11·175	16·362

acid nitroso-sulphuric acid, so long as there is oxygen in excess and the atmosphere contains more N_2O_3 than corresponds to the tension of the acid in question at that special temperature (*cf.* above). Otherwise reduction to NO takes place. Acids below sp. gr. 1·600 are able to fix N_2O_3 under the same conditions, but only at comparatively low temperatures; at higher temperatures there is reduction even in the presence of an excess of O and N_2O_3.

The previously mentioned *blue or purple acid*, formed by the action of reducing substances on nitroso-sulphuric acid, and sometimes occurring in vitriol chambers, is, according to Sturac-

4. *Acid of Sp. Gr.* 1·60 (*say*, 69 *per cent.* H_2SO_4).

N_2O_3 originally present. Grammes in 1 litre	Loss of N_2O_3 in grammes per litre at				
	50°.	60°	70°.	80°.	90°.
1	0·050	0·086	0·175	0·336	0·412
2	0·100	0·236	0·436	0·725	0·912
3	0·325	0·525	0·775	1·150	1·500
4	0·562	0·836	1·250	1·910	2·100
5	0·812	1·150	1·500	2·120	2·700
6	1·050	1·450	1·900	2·500	3·350
7	1·286	1·800	2·350	3·100	4·112
8	1·512	2·150	2·800	3·725	4·900
9	1·750	2·125	3·250	4·336	5·686
10	1·975	2·812	3·712	4·900	6·475
11	2·250	3·162	4·436	5·265	7·300
12	2·512	3·536	4·675	6·325	8·125
13	2·786	3·936	5·150	7·012	8·962
14	3·065	4·250	5·650	7·700	9·750
15	3·360	4·612	6·125	8·400	11·625
16	3·600	4·975	6·612	9·125	11·462
17	3·862	5·350	7·100	9·525	12·250
18	4·150	5·712	7·600	10·462	13·136
19	4·425	6·075	8·086	11·350	13·975
20	4·700	6·425	8·562	11·850	14·800

zewski and Zbijewski, a product of the reduction of nitrous vitriol by SO_2, which they call "nitrosylic acid." It can be reduced still further by SO_2, as first asserted by Wentzki and then revoked by him (*Z. angew. Chem.*, 1911, p. 392). This product would be "hyponitrosylic acid" (*Oesterr. Chem. Zeit.*, xiv. 235; *Chem. Cbl*, 1911, ii. p. 1558).

Another reducing agent whose action had formerly been overlooked is *carbon*, in the shape of the *coke* employed for packing the Gay-Lussac tower. I have shown (*J. Soc. Chem. Ind.*, 1885, p. 31) that coke has a very strong reducing-action on nitric acid dissolved in sulphuric acid, which goes far towards explaining the fact that the "nitrous vitriol" from the Gay-Lussac towers never, except under altogether exceptional circumstances, contains any nitric acid, even when considerable quantities of N_2O_4 had been present in the exit gases. But the reduction goes further; some N_2O_3 itself, in the shape of nitroso-sulphuric acid, is by the coke reduced to lower nitrogen oxides and is thus lost. This has been proved by myself in my laboratory (*Z. angew. Chem.*, 1890, p. 195); and as it is a matter of importance, we give the results obtained in the following table:—

Material used.	Temperature ° C.	Time (hours).	Original percentage in N_2O_3, grammes.	Percentage decrease.	
				In grammes N_2O_3.	Of the N_2O_3 originally present.
1. Nitrous Vitriol of sp. gr. 1·8375.					
Gas Coke in lumps . .	15	24	18·93	0·330	1·71
" " . .	14	2	18·92	0·539	2·86
" " . .	70	2	19·30	0·742	3·84
Oven Coke in lumps .	15	24	19·30	0·285	1·48
" " . .	40	2	18·92	0·362	1·91
" " . .	70	2	19·30	0·452	2·34
Gas Coke in powder . .	15	24	19·30	0·790	4·09
" " . .	40	2	18·92	0·858	4·54
" " . .	70	2	16·22	0·903	5·57
" " . .	100	2	16·22	4·611	28·43
Oven Coke in powder .	15	24	19·30	0·379	1·96
" " . .	40	2	18·92	0·451	2·38
" " . .	70	2	16·22	0·527	3·25
" " . .	100	2	16·22	2·770	17·08
2. Nitrous Vitriol of sp. gr. 1·725.					
Gas Coke in powder . .	15	24	19·50	0·333	1·98
" " . .	40	2	19·50	0·574	2·94
" " . .	70	2	19·50	0·891	4·57
" " . .	100	2	19·50	3·410	17·49

We see from it that at 40° C. two hours' contact reduced the percentage of N_2O_3 by 2·4 to 4·5 per cent.; at 70° the reduction sometimes went as far as 28 per cent. The latter temperature ought never to occur in a Gay-Lussac tower, but it does occur regularly in Glover towers up to the top. The conclusion is that coke-packing should be entirely avoided in Glover towers, and that it is not advisable even for Gay-Lussac towers (*cf.* Chapter VI.).

ANALYSIS OF SULPHURIC ACID.

Qualitatively sulphuric acid is always best recognised by the white precipitate of barium sulphide which it gives with barium chloride, both in the free state and in the solutions of its salts, even when very much diluted. This precipitate mostly settles down as a heavy powder, but in extremely dilute liquids occasionally appears only after some little time as a white cloud. Barium sulphate is practically insoluble in water, solutions of salts, and free dilute acids; in concentrated acids it is a little soluble, especially on heating, also in concentrated sulphuric acid itself and in solutions of ferric chloride. On the other hand, in a very concentrated liquid free from sulphuric acid, but containing much hydrochloric or, especially, nitric acid, the addition of barium chloride may cause a precipitate of barium chloride itself or of barium nitrate, which, however, is distinguished from barium sulphate by its crystalline appearance, and even more by vanishing on dilution of the liquid; barium seleniate is distinguished from barium sulphate by its solubility on boiling with concentrated hydrochloric acid, and by its behaviour before the blowpipe. The barium chloride reaction proves the presence of sulphuric acid either in its free state or in its salts. In order to find sulphuric acid in the *free* state in the presence of sulphates of acid reaction, either the alcoholic solution of the substances can be tested with barium chloride (free acid being soluble, but all sulphates insoluble in absolute alcohol); or the charring properties of concentrated oil of vitriol are made use of by evaporating the solution mixed with a little cane-sugar in a small porcelain capsule on the water-bath, and observing whether a blackening of the sugar takes place. This reaction, however, also takes place with the sulphates of very weak bases, such as alumina or ferric oxide; nor can sulphuric acid be distinguished with certainty in this way from hydrochloric or nitric acid; but in phosphoric, acetic, tartaric acid, etc., a very small proportion of sulphuric acid can be proved by this reaction. Another reaction for free sulphuric acid, as well as for any other strong free acid, is that with methyl-orange: the latter does not change colour by adding metallic salts, but is changed by the smallest quantity of free sulphuric acid.

In insoluble sulphates the acid is recognised by fusing them with alkaline carbonates, or by boiling with concentrated solutions of the same and filtering the solution of the alkaline sulphate formed thereby from the insoluble carbonates, or with the blowpipe, on charcoal, by the formation of sodium sulphide, according to well-known methods.

The *quantitative estimation* of *free* sulphuric acid for technical purposes is almost exclusively effected by volumetric methods or by the hydrometer. In both cases, of course, impurities will have a disturbing action; but for technical purposes their influence on the estimation of sulphuric acid may nearly always be neglected (*cf.* pp. 303 *et seq.*). The hydrometric estimation of sulphuric acid has been already described in detail on pp. 299 *et seq.*; and we shall here only point out again that the temperature must not be neglected in this case.

The volumetrical estimation of free acid generally takes place by means of a standard solution of potash, soda, or ammonia. According to the degree of accuracy required, either a normal solution is used (that is, one containing per litre an equivalent expressed in grammes), or a semi- or decinormal solution, etc.

Formerly tincture of litmus was most frequently used as indicator. Litmus is not well adapted for working in artificial light: in this the red appears almost as clear as water, the blue like a dark violet; but the transition from bright red into purple, etc., cannot be seen with certainty. This can be remedied by monochromatic light, if the artificial light is coloured yellow by common salt: the red appears clear as water, the blue like deep black; and the transition is even sharper than in daylight.

Litmus has, moreover, the disadvantage that it is sensitive to all weak acids as well, and that it is destroyed by sulphuretted hydrogen. If, therefore, carbonates are to be tested with it, this must be done at a boiling heat, and the boiling must be prolonged for some time. If any sulphides are present, an excess of acid must be added, and all the H_2S expelled by prolonged boiling; only then should the litmus be added, and the analysis finished by retitrating. This makes the application of litmus very troublesome in alkalimetry; in fact a real error is introduced by the necessity of long boiling, if this is done in glass vessels which yield up some alkali thereby. In acidimetry this drawback is less felt, but only when the standard alkali is kept entirely free from carbonates, which is very difficult in the daily practice of alkali works.

Phenolphthalein has in many cases taken the place of litmus. It is one of the most sensitive indicators known, and the change from no colour in acid solutions to a decided pink when the faintest trace of free alkali is present, is easily noticed even in artificial light. But this indicator has two drawbacks: it is too sensitive even towards the weakest acids (*e.g.* CO_2), and it fails in the presence of ammonia. The former circumstance entails exactly the same difficulties as in the case of litmus. Hence, while phenolphthalein is the best of all indicators for titrating weak acids, it is decidedly inferior to methyl orange for the titration of alkalies containing carbonates or sulphides, and in the acidimetry of strong acids.

The indicator which in alkali and acid works is now universally employed is *methyl-orange*.[1] This is sulphobenzene-azodimethyl-aniline, or the sodium salt of this compound:

$$(SO_3Na)\ C_6H_4 - N_2 - C_6H_4\ N(CH_3)_2,$$

which is employed in an aqueous solution of 1 in 2000 water, or even more dilute, and a very small quantity of the solution is used for each test. It is best kept in a bottle with a perforated cork, a glass tube drawn out to a point and inserted in the cork serving as a pipette for regulating the supply. Methyl-orange is orange in neutral solutions or in the presence of free alkali, but is faintly yellow in very dilute solutions, and no more ought to be added to the liquid to be tested than suffices to colour it just perceptibly yellow. In this case a single drop of fifth-normal sulphuric or hydrochloric acid will cause a transition into red. But when too much of the indicator has been added, so that the colour of the solution is orange, the transition into red (or, rather, in this case into pink) is only gradual, and the test is spoiled. Warm solutions behave in a similar manner. It is therefore a distinct rule to be observed with methyl-orange, to employ as little as possible of it, and to work always at the ordinary temperature. This is made possible by the fact that methyl-orange is not acted upon by weak acids, such as CO_2, H_2S, acetic acid, etc.; and this is undoubtedly one of its most valuable properties, since the trouble and loss of time in boiling the liquids, and the error introduced in the case of glass vessels (which easily give up some alkali to the hot liquid) are thereby avoided. Both Na_2CO_3 and $NaHCO_3$ can be titrated directly in the cold just as well as NaOH, the total available soda being always indicated. Sulphurous acid behaves in the manner explained *suprà* (p. 275), that is, the compound Na_2SO_3 is alkaline, $NaHSO_3$ neutral, to methyl-orange. Oxalic acid, as well as other strong organic acids, come in between sulphurous acid and the strong mineral acids; no sharp results can be obtained with them, and hence oxalic acid cannot serve as standard acid with methyl-orange. On the other hand, ammonia, which cannot be titrated with phenolphthalein, behaves quite normally towards methyl-orange, just like potash and soda. The normal sulphates of peroxide of iron, alumina, etc., which give an acid reaction with litmus, are neutral towards methyl-orange, so that any free acid present with them can be estimated by means of this indicator.

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[1] I have proposed this name for the indicator introduced by me, in lieu of the commercial names of Poirrier's Orangé No. III or helianthin (*Chem. News*, xliv. p. 288); and it has been generally adopted.

Methyl-orange is destroyed by nitrous acid. Nevertheless it can be easily employed in titrating sulphuric or nitric acid containing nitrous acid in two ways: either by adding the indicator shortly before the saturation is completed and quickly finishing the titration, or by supersaturating the acid with caustic soda and retitrating with standard acid.

Nitrous acid acts upon methyl-orange like a strong mineral acid, and is therefore completely saturated before the pink colour has changed to yellow, if there is not time for the colouring-matter to be destroyed.

The tropæolins, formerly recommended as indicators, are nothing like so sensitive as methyl-orange, and are best not used at all as indicators, especially since several totally distinct compounds are comprised under this name, and the dealers do not always supply that which is really wanted.

In the titration of sulphuric acid recovered from the "*vitriol-tar*" produced in refining petroleum, etc., all indicators yield erroneous (too high) results, as they are affected also by the sulphonic acids present (Hausmann in *Petroleum*, 1911, p. 2301).

Free sulphuric acid (including that contained in commercial ferric or aluminium sulphate, or any other sulphate) is estimated by adding a drop of methyl-orange solution, which produces a pink colour, and then adding a standard solution of alkali, till the pink tint has changed into pure light yellow. It is best to check this by reproducing the faint pink shade by means of a drop of standard acid.

The normal alkaline solution itself is best standardised by means of a normal acid, be it sulphuric or hydrochloric acid; and this on its part is best standardised by pure ignited sodium carbonate, which is easily obtained or prepared—for instance, by washing and igniting sodium bicarbonate. Since, by excessive heating, traces of sodium oxide may be formed, it is best to merely heat the bicarbonate at 300° C. during an hour. If sodium carbonate, bought as chemically pure, dissolves in water without any residue, and shows by the ordinary reagents no chloride or sulphate, or only unweighable traces of these, it can be used at once for standardising normal acids after moderately igniting. If methyl-orange is used as indicator, this roundabout way need not be taken, especially at works' laboratories, but pure sodium carbonate itself can be used as acidimetrical liquid, either in a normal solution containing 53 g. per litre or in more dilute solutions. The latter are more to be recommended, since the really normal solution causes efflorescences of sodium carbonate at the lower ends of the burettes, etc., which does not happen with semi-normal or weaker solutions, at least not for some time.

Although it is more important in alkalimetry than in acidimetry, we will here treat of the *standard acid* itself. As such many factory-chemists use sulphuric acid, but we recommend as more suitable hydrochloric acid, both because it can be used for estimating alkaline earths as well, and because it admits of a twofold way of checking the standard, either volumetrically by pure sodium carbonate, or gravimetrically by argentic nitrate. The gravimetric estimation of sulphuric acid by barium chloride is nothing like so accurate as the estimation of HCl in the shape of AgCl. Oxalic acid, most strongly recommended by Mohr, and formerly used by very many chemists, has great drawbacks. It is extremely difficult to prepare in the perfectly pure and dry state, without losing some of the water of crystallisation; it does not keep in weak solutions, and it cannot be employed with methyl-orange.

For standardising normal acids, sometimes a solution of pure sodium carbonate is made, of which portions are taken out with a measuring-pipette. For the most accurate estimations it is, however, always preferable to *weigh* each portion of sodium carbonate, directly after igniting and cooling, into the beaker, since it is never possible to measure as accurately as to weigh, because, among other reasons, the volumetrical apparatus very rarely agree quite accurately one with another. In spite of the trouble, it should most certainly not be neglected to compare, in the first instance, the pipettes with all the measuring-flasks, in order to see whether the former fill the latter precisely; secondly, to calibrate the burettes accurately, in which case it will often be found that the upper parts differ sensibly from the middle and lower parts, which causes a corresponding error. Of course the burettes must again be compared with the other measuring-apparatus.

The standard acid is made to represent *equivalents*, not molecules; that is, if sulphuric or oxalic acid, it will contain one-half of the molecular weight in grammes, viz., 49·04 or 63·03 g., because these acids are bivalent; but if it is the univalent hydrochloric or nitric acid, it will contain the total molecular weight, viz., 36·46 g. HCl, or 63·02 g. NO_3H. First of all, the acid is diluted a little less than necessary, and it is found out how many cubic centimetres of it are required for a certain quantity of sodium carbonate. From this the quantity of water is computed which is required for obtaining an exactly normal acid; and after mixing this with the acid the accuracy of the standard is ascertained by repeated titration with sodium carbonate. Not less than 2 to 3 g. of the latter should be taken for each test. If litmus is to be the indicator, to the alkaline solution drops of tincture of litmus are added till it becomes very markedly blue, then acid till strong effervescence sets in; and the liquid is now made to boil; then to the hot liquid gradually more and more acid is added, till the blue colour has passed through the purple and reddish purple of the CO_2 reaction to the bright red of the SO_4H_2 reaction. The liquid cooled by the addition of acid must be constantly heated again. Often, after several minutes boiling, the apparently red liquid again turns purple and then blue. When working with boiling liquids there is never any doubt, to a single drop, respecting the point where the pure red sets in. The test must be made in a porcelain capsule, not in a glass beaker, since the glass may yield some alkali to the boiling liquid. Precisely the same troublesome method must be employed with phenolphthalein. All this trouble is saved by using methyl-orange as indicator and working in the cold.

When a perfectly accurate normal acid has been obtained, the normal alkali, whether ammonia, soda, or potash, is most easily made from it; and this is now used for the acidimetric test of sulphuric acid. Concentrated sulphuric acid must, of course, first be diluted in the usual manner.

The estimation of sulphuric acid *in sulphates* has been described *suprà*, p. 92, when treating of the analysis of pyrites.

Analysis of Fuming Oil of Vitriol.

Several publications have been made on this subject, *e.g.* by Furstenau (*Chem. Zeit.*, 1880, p. 18), Moller (*ibid.*, p. 569), Becker (*ibid.*, p. 600), Winkler (*Chem. Ind.*, 1880, p. 194), Clar and Gaier (*ibid*, 1881, p. 251). We shall, in the first instance, principally describe the methods contained in Lunge's *Technical Chemists' Handbook*, pp. 143-145, as derived from practical information, with a few improvements.

In the present case even the *taking of the sample* is not quite a simple task. Measuring it in a pipette is out of the question; it must be weighed. But even for this purpose the article, if solid, must be first liquefied. This is comparatively easy with partly crystallised acid or with solid pyrosulphuric acid; these can be liquefied without any danger in a closed vessel by gently heating to 30° in a sand-bath. Soldered-up tins are generally placed in a suitably heated stove. There is no sensible loss of strength if the aperture for this purpose is previously opened and at once covered with a watch-glass. This prevents the production of any pressure within the vessel during the heating, which must otherwise be guarded against in opening it. The case is different with products containing a larger percentage of anhydride. These do not liquefy completely, a portion always remaining in the state of a gelatinous residue. This residue is, however, composed exactly like the liquid portion, so that the sample may be taken out of the latter without any danger of making a mistake.

The sample is weighed either in glass bulbs or in a glass tap-tube. The former (proposed by Clar and Gaier) are very thin bulbs of about $\frac{3}{4}$ inch diameter, ending each way in a capillary tube (Fig. 52). The liquefied acid (2 or 3 g.) is sucked into the bulb, without danger to the operator, by means of a bottle closed with an india-rubber cork, through which passes a tightly-fitting glass tap, connected at its free end with an elastic tube. Suction is applied to the latter, the tap is closed, the elastic tube is drawn over one of the capillary ends of the weighing-bulb, and by opening the tap a sufficient quantity of acid is admitted into the bulb.

The capillary tube is cleaned and one of the two ends is sealed at the lamp. The other end can be left open without fear of any loss of SO_3, or attraction of moisture during weighing. The weighing is best done on a small platinum crucible with two nicks, on which the ends of the bulb can rest. If the latter should be accidentally broken, the acid runs into the crucible, not on the balance. Then the bulb, open end downwards, is put into a small Erlenmeyer flask, into the neck of which it should fit exactly (Fig. 52), and which contains so much water that the capillary tube dips pretty far into it to prevent any loss of SO_3 on mixing the acid with water. Now break off the other point, allow the acid to run out, squirt a few drops of water into the upper capillary, and ultimately rinse the whole bulb-tube by repeated aspiration of water. Dilute the liquid to 500 c.c. and take 50 c.c. for each test. The testing is performed with fifth-normal solution of soda (1 c.c. = 0·008006 g. SO_3) and litmus or methyl-orange as indicator. The acidity found is diminished by that proceeding from SO_2, found by titrating another sample with iodine.

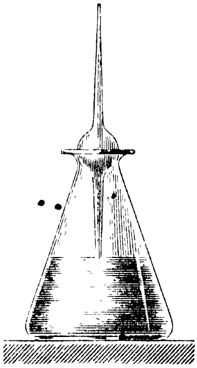
FIG. 52.

In place of the bulb-tube we prefer the glass tap-tube, as shown in Fig. 53. The tap should be tight without greasing, and the tube below it should taper gradually. It is charged by suction, in the same way as described above, with about 0·5 g. of Nordhausen acid, no more, in order to be able to titrate it directly, without taking an aliquot portion. After the proper quantity of acid has been introduced, the tap is closed, the tube is cleaned outside with filtering paper, and it may be weighed at once, without any fear of a change of weight during the operation. It is, however, preferable to employ a tube (as shown in Fig. 54) ground into an outer glass case, which is, of course, tared together with the empty tube.

After weighing, place the tube point downwards in water, or, in the case of nearly pure anhydride or the strongest Nordhausen acids, in a layer of crystallised, coarsely powdered Glauber's salt, and slowly run out the contents. Then squirt a drop of water from above into the tube, allow it to stand for a moment, and rinse thoroughly with water. Anhydride once melted for the purpose of filling the tube remains liquid enough to complete the weighing and running out without requiring to be heated again.

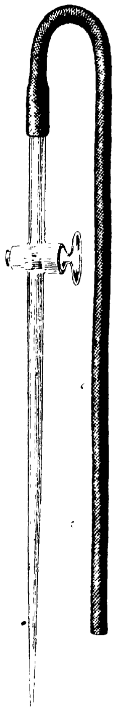

FIG. 53.

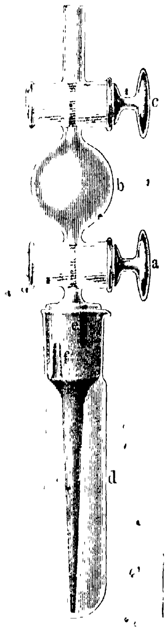

FIG. 54.

The most convenient apparatus for weighing off fuming sulphuric acid (as well as other fuming-acids or substances evolving vapours) is the "bulb-tap pipette," constructed by Lunge and Rey (*Z. angew. Chem.*, 1891, p. 165), and shown in Fig. 54, in which both the filling as well as the weighing and discharging are performed without any loss of vapours and without requiring any special aspirating apparatus. Above the tap *a* there is a bulb *b*, rather less than an inch in diameter, and above this a second tap *c*. The lower portion of the pipette is ground into a glass tube *d*, closed at the bottom. In the conical part of the pipette there is a groove *e*, reaching half-way down, the corresponding half of the groove *f* being in the outer tube. By turning the pipette in the latter, the tube *d* can be made to communicate with the outer air, or the reverse. When the pipette is to be used, close tap *a*, suck at the top with the mouth, and before leaving off shut tap *c*, so that the bulb *b* contains a partial vacuum. Dip the point of the pipette into the acid and open *a*; the acid will rise up, but *a* is shut before it gets so far, or even sooner, when enough has got in. Clean the pipette outside, put it into *d*, and weigh. In most ordinary cases (with other acids, ammonia, etc.) the grooves *e* and *f* are made to communicate; water is squirted through *c* into *b* and then run through *a*, with the contents of the pipette, into *d*, the air escaping through *e* and *f*. The dilute acid is run into a beaker and titrated. In the case of Nordhausen acid it is preferable to take the pipette out of *d*, rinse the latter into a beaker, run the contents of the pipette, by opening *a*, into water or Glauber's salt contained in the same beaker, then squirt water through *c* (during which time *a* may be closed), and rinse the pipette into the same beaker. The sucking at *c* is quite sufficient to produce the necessary rarefaction of air in *b*, and no vapours are lost, as is inevitable with any other kind of aspiration.

Very strong oleum (70 per cent. SO_3 and upwards) is best weighed in glass bulbs (p. 358) sealed at both ends; these are put into a bottle containing sufficient water, which is closed by a ground-in stopper; the bulb is smashed by shaking the bottle, and the titration is made.

Brewster (*J. Amer. Chem. Soc*, 1907, p. 1376) recommends running the sample, taken by a Lunge pipette, by means of a small glass tube, bent at a right angle at the bottom, into a small Erlenmeyer flask, containing 15 c.c. water, and washing the tube with a little water. The results are concordant up to 0·05 per cent.

Finch (*J. Soc. Chem Ind.*, 1910, p. 625; *Z. Schiess- und Sprengwesen*, 1910, p. 167) describes an apparatus for weighing off fuming O.V. Vernon (*Chem. Zeit.*, 1910, p. 792; *J. Soc. Chem. Ind.*, 1910, p. 1007) describes an improvement on this apparatus.

The sampling of solid sulphuric anhydride is not an easy matter. This substance, which is now a regular article of trade and is sent out in iron bottles, is much too compact and tough to enable a sample to be taken out by means of an auger. Before using it, the iron bottles are always heated in a stove till the anhydride has completely liquefied; but in this state the bottle on opening emits such a dense cloud of fumes that any sampling is out of the question. The way out of the difficulty is this:—In a stoppered bottle some lumps of the solid anhydride are weighed off on a large balance and are then mixed with a sufficient quantity of accurately analysed monohydrated sulphuric acid, to form an acid of 70 per cent. SO_3, which is liquid at ordinary temperatures. The solution is promoted by gently heating the bottles, say to 30° or 40° C., with the stopper loosely put on. At last a sample is taken out by means of the pipette described above (p. 360) and the analysis performed in the usual way, taking account of the slight proportion of water present in the "monohydrate" employed.

Rosenlecher (*Z. anal. Chem.*, xxxvii. p. 209) describes the method employed at Freiberg. A number of bulbs are made from a glass tube, 6 or 8 mm. wide, of the form shown in Fig. 55, and keeping them exactly to the dimensions indicated. The capillary ends are contracted before a spirit-lamp to ½ mm. bore, in the case of very strong anhydride to ¼ mm. The bulbs are

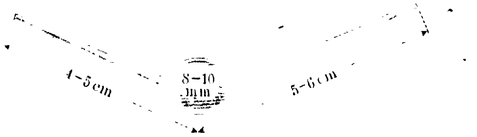

FIG. 55.

filled by aspiration by means of a capillary rubber tube drawn over the shorter end, in case of need interposing a test-tube filled with soda crystals. The suction is continued until the acid arrives in the bulbs, before the heavy fumes enter the shorter capillary. All the bulbs are turned with the points of the capillaries upwards, cleaned outside, and placed in a pasteboard box provided with nicks. The weighing is performed in a platinum crucible (p. 359) or on a specially made wire stand. No attraction of moisture need be feared during the weighing, but the bulbs must not be heated by touching them with the fingers. They are then placed in stoppered bottles, charged with 20 or 30 c.c. water of ordinary temperature and the indicator, in such manner that the acid does not flow out. The wetted stopper is put tightly in, the bottles are placed sideways (up to this time the colour of the indicator should not have changed), the bulbs broken by shaking, and then, after the white fumes have vanished, the titration is performed in the bottle itself.

Gaunt, Thomas, and Bloxam (*J. Soc. Chem. Ind.*, 1907 p. 1175) describe in detail the method for sampling and titrating fuming sulphuric acid, employed by Dr Messel.

The results of titration are first calculated for the total (combined and uncombined with water) SO_3, each cubic centimetre of normal soda solution indicating 0·040 g. SO_3, and the proportion of free SO_3 and H_2SO_4 present is then read off by means of the following formula: $SO_3 = S - 4{\cdot}444\ (100 - S)$, in which SO_3 denotes the free sulphur trioxide, and S the total SO_3 as found by titration.

This calculation is saved by the following table, computed by Knietsch (*Ber.*, 1901, p. 4114):—

SO_3		SO_3		SO_3		SO_3		SO_3		SO_3	
Total.	Free.	Total	Free.	Total.	Free.	Total	Free	Total	Free	Total.	Free
81·63	0·0	84·7	16·7	87·8	33·6	90·9	50·5	94·0	67·3	97·0	83·7
81·7	0·4	84·8	17·2	87·9	34·1	91·0	51·0	94·1	67·9	97·1	84·2
81·8	0·9	84·9	17·8	88·0	34·7	91·1	51·6	94·2	68·4	97·2	84·8
81·9	1·5	85·0	18·3	88·1	35·2	91·2	52·1	94·3	69·0	97·3	85·3
82·0	2·0	85·1	18·9	88·2	35·8	91·3	52·6	94·4	69·5	97·4	85·8
82·1	2·6	85·2	19·4	88·3	36·3	91·4	53·2	94·5	70·1	97·5	86·4
82·2	3·1	85·3	20·0	88·4	36·8	91·5	53·7	94·6	70·6	97·6	86·9
82·3	3·6	85·4	20·5	88·5	37·4	91·6	54·3	94·7	71·2	97·7	87·5
82·4	4·2	85·5	21·0	88·6	37·9	91·7	54·8	94·8	71·7	97·8	88·0
82·5	4·7	85·6	21·6	88·7	38·5	91·8	55·4	94·9	72·2	97·9	88·6
82·6	5·3	85·7	22·2	88·8	39·0	91·9	55·9	95·0	72·8	98·0	89·1
82·7	5·8	85·8	22·7	88·9	39·6	92·0	56·4	95·1	73·3	98·1	89·7
82·8	6·4	85·9	23·2	89·0	40·1	92·1	57·0	95·2	73·9	98·2	90·2
82·9	6·9	86·0	23·8	89·1	40·6	92·2	57·5	95·3	74·4	98·3	90·7
83·0	7·5	86·1	24·3	89·2	41·2	92·3	58·1	95·4	75·0	98·4	91·3
83·1	8·0	86·2	24·9	89·3	41·7	92·4	58·6	95·5	75·5	98·5	91·8
83·2	8·5	86·3	25·4	89·4	42·3	92·5	59·2	95·6	76·1	98·6	92·4
83·3	9·1	86·4	26·0	89·5	42·8	92·6	59·7	95·7	76·6	98·7	92·9
83·4	9·6	86·5	26·5	89·6	43·4	92·7	60·3	95·8	77·1	98·8	93·5
83·5	10·2	86·6	27·0	89·7	43·9	92·8	60·8	95·9	77·7	98·9	94·0
83·6	10·7	86·7	27·6	89·8	44·5	92·9	61·3	96·0	78·3	99·0	94·6
83·7	11·3	86·8	28·1	89·9	45·0	93·0	61·9	96·1	78·8	99·1	95·1
83·8	11·8	86·9	28·7	90·0	45·6	93·1	62·4	96·2	79·3	99·2	95·6
83·9	12·3	87·0	29·2	90·1	46·1	93·2	63·0	96·3	79·9	99·3	96·2
84·0	12·9	87·1	29·8	90·2	46·6	93·3	63·5	96·4	80·4	99·4	96·7
84·1	13·4	87·2	30·3	90·3	47·2	93·4	64·1	96·5	81·0	99·5	97·3
84·2	14·0	87·3	30·9	90·4	47·7	93·5	64·6	96·6	81·5	99·6	97·8
84·3	14·5	87·4	31·4	90·5	48·3	93·6	65·2	96·7	82·0	99·7	98·4
84·4	15·1	87·5	31·9	90·6	48·8	93·7	65·7	96·8	82·6	99·8	98·9
84·5	15·6	87·6	32·5	90·7	49·4	93·8	66·2	96·9	83·1	99·9	99·5
84·6	16·2	87·7	33·0	90·8	49·9	93·9	66·8				

This table serves also for the frequently performed operation of mixing Nordhausen acid of a certain percentage of SO_3 with concentrated sulphuric acid, in order to produce an acid with a smaller percentage of SO_3. This can be done by means of a formula given by Gerster (*Chem. Zeit.*, 1887, p. 3),

$$x = 100\frac{b-a}{a-c},$$

where x represents the quantity of sulphuric acid which must be added to 100 parts of the Nordhausen acid; a the total sulphur trioxide in 100 parts of the acid desired; b the total SO_3 in 100 parts of the Nordhausen acid to be diluted; c the total SO_3 in 100 parts of the ordinary acid to be used for diluting The values of a and b are taken from the preceding table; c is easily calculated by multiplying the percentage of H_2SO_4 with $\frac{80}{98}$ or 0·816. An example will make this clearer. Supposing there is a Nordhausen acid of 25·5 per cent. SO_3 in stock, as well as sulphuric acid of 98·2 per cent. H_2SO_4, and an acid of 19 per cent. SO_3 is required, we have then :—

$$a = 85.1;\ b = 86.3;\ c = 98 \times 0.816 = 80.1.$$

$$x = 100\frac{b-a}{a-c} = 100\frac{86.3-85.1}{85.1-80.1} = \frac{120}{5} = 24.$$

That is: by mixing 100 parts of acid of 25·5 per cent. SO_3 with 24 parts of sulphuric acid of 98·2 per cent. H_2SO_4, Nordhausen acid is obtained containing 19 per cent. SO_3. [In reality the strength of the mixed product will be slightly below that calculated, since a certain loss of SO_3 is hardly avoidable in the manipulation.]

Prals (*Chem. Zeit.*, 1910, p. 264) gives a formula for *preparing Nordhausen acid of given strength.* a denotes the quantity to be prepared, h the percentage of SO_3 required, x the weight of the Nordhausen acid to be used, with k per cent. SO_3, y the weight of the ordinary acid to be mixed with the Nordhausen acid of s per cent. SO_3:

$$(1)\ x = a \times \frac{9h + 40(100 - s)}{9k + 10(150 - s)}.\qquad (2)\ y = a - x = a\frac{9(k-h)}{9k + 40(100 - s)}.$$

For sulphuric acid sp. gr. 1·840 = 95·60 per cent. H_2SO_4, 100

$-s$ is $=4·4$. If we assume 4·5 to simplify the formula, equations (1) and (2) become:

$$(3)\ x = a \times \frac{h+20}{k+20}. \qquad (4)\ y = a \times \frac{k-h}{k+20}.$$

Nordhausen acid generally contains some *sulphurous acid* which must be tested for and deducted from the total acidity, in order to find the sulphuric acid present. In *Z. angew. Chem.*, 1895, p. 221, I have drawn attention to the fact that in allowing for the SO_2 sometimes a serious mistake is committed. The SO_2 is always tested for by iodine solution, and is then subtracted from the total acidity. Here we must consider that the neutrality-point in the case of phenolphthalein is reached when $1SO_2$ has been combined with 2NaOH, but in the case of methyl-orange only 1NaOH is consumed for $1SO_2$. Litmus cannot be used at all, as it gives uncertain results between these two limits. With methyl-orange 1 c.c. normal soda solution indicates 0·040 g. SO_3, but 0·064 g. SO_2. Hence for each cubic centimetre of decinormal iodine solution only 0·05 c.c. of normal or 0·1 c.c. of seminormal solution of NaOH must be deducted. If this is overlooked, a very serious mistake is committed; for since everything which is not present as SO_3 or SO_2 is assumed to be water, the incorrect allowance for SO_2 will cause not merely a deficiency of SO_3, but a surplus of H_2O; and as this must be represented as combined with 4·444 its weight of water, far too little free SO_3 is found.

A practical instance will illustrate this. 3·5662 g. fuming acid were diluted to 500 c.c. and 100 c.c. (=0·71124 g.) employed for each test. This consumed 5·40 c.c. iodine solution $= 5·40 \times 0·0032 = 0·01728$ g. SO_2 or 2·43 per cent. SO_2. On titrating with seminormal soda solution and methyl-orange, 34·40 c.c. was used. By erroneously deducting $0·2 \times 5·40 = 1·08$ c.c., there remained 33·32 c.c. $=0·6664$ g. SO_3 or 93·70 per cent. The fuming acid therefore would have contained 93·70 per cent. SO_3, 2·43 SO_2, 3·87 H_2O. The 3·87 H_2O is $= 17·20$ SO_3, and the *free* SO_3 would be $=93·70-17·20=76·50$ per cent.

In reality the 5·40 c.c. decinormal iodine corresponds to only 0·54 c.c. seminormal soda, leaving 32·86 c.c. $=0·6772$ g. $SO_3 =$ 95·21 per cent. Composition of the acid: 95·21 per cent. SO_3, 2·43 SO_3, 2·36 H_2O. The 2·36 H_2O is $= 10·49$ SO_3, leaving 95·21

−10·49 = 84·72 per cent. free SO_3. Hence by that erroneous calculation the factory committed an error of 8·25 per cent. to its own disadvantage!

Exactly the same result is obtained when performing the calculation by means of Knietsch's table, *suprà*, p. 363.

We have, as already mentioned, assumed everything as H_2O which has not been found to be present as SO_3 and SO_2. But it is advisable to estimate the *fixed impurities* as well, since otherwise their weight, multiplied by 4·444, is erroneously deducted from the free SO_3.

Setlik (*Chem. Zeit.*, 1889, p. 1670) proposes to substitute the following method for the titration of Nordhausen acid by caustic-soda solution:—Fifty or 100 g. are weighed out in a long-necked flask, and water is dropped in very slowly from a burette, divided into $\frac{1}{10}$ c.c., till the fuming has ceased. During the operation the flask must be well cooled. In order to observe the finishing point, the flask must be agitated after adding each drop of water till the fumes have been entirely absorbed by the acid. When no fumes whatever are formed at the surface and a drop, falling into the middle of the acid, dissolves quietly, the end is reached. Acid of more than 35 per cent. SO_3 must be previously diluted with monohydrated sulphuric acid. Setlik claims that this plan is much more expeditious and quite as exact as the alkalimetrical way; but the analytical proofs adduced by himself do not bear this out (there are deviations up to 0·9 per cent. SO_3), and we can regard his method only as a test for internal factory use, but not between buyer and seller.

Rabe (*Chem. Zeit.*, 1901, p. 345) estimates the strength of fuming (or ordinary) sulphuric acid by utilising the fact that Nordhausen acid loses its property of fuming in contact with air as soon as all its SO_3 has been converted into SO_4H_2 by the water present in ordinary sulphuric acid containing less than 100 per cent. SO_4H_2:

$$aH_2SO_4 + cH_2O + bH_2SO_4 + cSO_3 = aH_2SO_4 + bH_2SO_4 + cH_2SO_4.$$

We require, to begin with, to know the percentage of a certain sample of strong chemically pure sulphuric acid, say 95 per cent. H_2SO_4 + 5 per cent. H_2O, which is ascertained in the usual way by titration. This acid we run from a glass-tap burette into a beaker containing 25 c.c. of Nordhausen acid, repeatedly agitating and blowing upon the acid (cooling is generally unnecessary), until the acid in the beaker does not form any more fumes on shaking. Suppose we require for this 24·8 c.c. of the acid *A*, containing 95 per cent. H_2O and 5 per cent. H_2O. If we wish to ascertain the strength of another sample (*B*) of concentrated ordinary acid, we run this from a burette into 25 c.c. of the same Nordhausen acid as before. Suppose we now require 30·5 c.c. of acid *B*; this proves that acid *B* contains $\frac{24\cdot8 \times 5}{30\cdot5} = 4\cdot07$ per cent. H_2O. If no impurities were present, this would mean a strength of 95·93 per cent. H_2SO_4.

On the other hand, the percentage of SO_3 in Nordhausen acid can be ascertained as follows:—Starting with *pure* (say, 30 per cent.) Nordhausen acid (*C*), we run in concentrated ordinary acid *D*, and find that 59·4 c.c. of acid *D* is required to make the fuming of 25 c.c. acid *C* disappear. We now try an unknown Nordhausen acid *E*, and find that 25 c.c. of it require 49·8 c.c. acid *D*. This gives us the proportion $30 : 59\cdot4 = x : 49\cdot8$ for the percentage of free SO_3 in acid *E*; $x = \frac{30 + 49\cdot8}{59\cdot4} = 25\cdot15$ per cent. SO_3. One c.c. of acid *D* had indicated $\frac{30}{59\cdot4} = 0\cdot505$ per cent. free SO_3; hence we need only multiply the cubic centimetres of acid *D*, required for suppressing the fumes of 25 c.c. of any unknown Nordhausen acid by the same coefficient, viz., 0·505.

Rabe's method yields very quick results, and is probably quite suitable for rough tests in the ordinary routine of acid-making. There is no weighing, only measuring, and any colour or opacity of the acids does not interfere with the test. But as the difference of specific gravities is neglected, this forms an element of uncertainty, and this is greatly increased by the evident difficulty of keeping a stock of exactly analysed and chemically pure concentrated and Nordhausen acid without any change. As commercial acids always contain certain impurities, these influence the results as well. The only real advantages of this method over that of Setlik are that no cooling is required during the operation, and that the large amount of concentrated acid is more accurately read off than the small amount of water, but otherwise Setlik's method is preferable.

H. Howard (*J. Soc. Chem. Ind.*, 1910, p. 3) describes a method for estimating the strength of fuming (and ordinary) sulphuric acid by means of the heat of reaction produced on dilution with water (*suprà*, p. 316).

Nordhausen acid is always sold by the percentage of uncombined sulphuric anhydride it contains (not taking any account of the pyrosulphuric acid, which is considered $= SO_3 + H_2SO_4$). Thus "30 per cent. Nordhausen acid" means a mixture of 30 parts by weight of SO_3 with 70 parts of H_2SO_4. The price of SO_3 is relatively higher in weak than in strong acids, as in manufacturing it the 5 or more per cent. of water contained in ordinary "rectified oil of vitriol" must be saturated with SO_3, each part of water requiring 4·444 parts of SO_3 to form H_2SO_4. It is therefore decidedly more advantageous to dilute strong Nordhausen acid with the strongest obtainable rectified O.V., or still better with monohydrated sulphuric acid.

Detection and Estimation of the Impurities of Sulphuric Acid.

The impurities of sulphuric acid are recognisable *qualitatively* in the following manner:—A *residue* found on evaporating sulphuric acid in a platinum crucible may contain sulphates of sodium (more rarely of potassium), of calcium, aluminium, iron, lead, copper, zinc, or other metals occur rarely in sensible quantity. *Ammonium* sulphate is sometimes present in somewhat large quantities (Gintl, *Chem. Zeit.*, 1879, p. 653). The individual substances are sought for by the ordinary analytical methods. *Iron* is already betrayed by the colour of the residue after ignition, and can also be detected in the acid itself, without evaporating it, by the ordinary reagents, such as potassium ferrocyanide, potassium sulphocyanide, etc. *Lead* is often found as a white precipitate of sulphate on diluting concentrated vitriol with water—further, by adding one or two drops of hydrochloric acid, by which white clouds are formed, which vanish on addition of more hydrochloric acid or on heating; with more certainty it is shown by diluting the acid with three or four times its volume of strong alcohol. The precipitate must, of course be examined further—for instance, with the blowpipe, by reduction on charcoal to metallic lead, by moistening with ammonium sulphide (which blackens it), etc.

Arsenic is recognised in (dilute) sulphuric acid by sulphuretted hydrogen; more delicate than this is Reinsch's test —diluting with equal volumes of water and pure hydrochloric acid, and immersing a bright copper foil, which, after gentle heating, is covered with a fast-adhering slate-grey precipitate, consisting of a compound of copper and arsenic, Cu_5As_2 (if the arsenic is present as arsenic acid, the reaction only sets in after longer heating). Most delicate is the detection of arsenic by Marsh's apparatus, in which, on addition of pure zinc and water, the arsenic is given off as arseniuretted hydrogen, and is found by reduction in a red-hot tube (Berzelius) or by lighting the gas and holding a piece of porcelain in the flame, on which any arsenic appears as spots. Since it is difficult to procure zinc absolutely free from arsenic, it is well to substitute aluminium foil for it. This test shows arsenic acid as well as arsenious acid; they can be distinguished by neutralising with ammonia and adding magnesia mixture: any precipitate thus formed must contain the arsenic acid, the filtrate the arsenious acid. Marsh's reaction is interfered with by the presence of sulphurous acid, nitrous acid, nitric acid, etc.

Selmi (*Gazz. Chim. Ital.*, x. p. 40) asserts that arsenic can be detected in acids which give no reaction by Marsh's test, by adding to 1000 g. of the acid 300 g. water and some lead chloride, distilling and testing the first portions of the distillate with sulphuretted hydrogen.

Seybel, and Wikander (*Chem. Zeit.*, 1902, p. 50) prove the presence of arsenic in sulphuric or hydrochloric acid by the yellow precipitate of AsJ_3, produced by the addition of a solution of potassium iodide. Sulphuric acid should be diluted to 45° B., hydrochloric acid should be employed in the concentrated state. The reaction is interfered with by free chlorine, ferric salts, nitrous acid (which equally cause a yellow coloration by the formation of free iodine), and by lead, which forms yellow PbJ_2. (Unfortunately commercial acids mostly contain one or the other of these impurities.)

According to Dawdow (*Chem. Centr.*, 1895, i. p. 811), Rosenheim (*Chem. News*, lxxxiii. p. 277), and Berry (*J. Soc. Chem. Ind.*, xx. p. 322), *selenium* interferes with the Marsh test. Schindelmeiser (*Chem. Centr.*, 1902, ii. p. 960) found that no AsH_3 is given off until all selenium has been precipitated by zinc or aluminium in the Marsh apparatus. Selenium, either as seleniate or selenate, also forms precipitates with potassium iodide very similar to AsI_3, so that Seybel and Wikander's test is also interfered with.

Although the minute rules laid down by the Arsenic Committee of the London Section of the Society of Chemical Industry (*J. Soc. Chem. Ind.*, 1902, p. 94) refer to the examination of beer, brewing-materials, food-stuffs, and fuels for arsenic, we shall reproduce here that portion of them which can be applied also to the examination of sulphuric acid. The Committee recommend to apply the Marsh-Berzelius test.

1. *Pure Reagents.*—To half a litre of "pure" sulphuric acid a few grammes of sodium chloride are added and the mixture is distilled from a non-tubulated retort, the first portion of about 50 c.c. being rejected. One volume of the distilled acid is diluted with 4 vols. of water. Zinc, free from arsenic, can be obtained from the dealers in fine chemicals. It should be regranulated by melting it and pouring it from some height into cold water. Mr A. H. Allen holds it to be essential that the zinc should contain a trace of iron.

2. *Apparatus.*—A bottle or flask, holding about 200 c.c., is fitted with a doubly-bored cork, india-rubber stopper, or with a ground-in glass connection, carrying a tapped funnel holding about 50 c.c. and an exit-tube. The latter is connected with a horizontal drying-tube, containing, first a roll of blotting-paper soaked in lead-acetate solution and dried, or a layer of cotton-wool prepared in a similar way, then a wad of cotton-wool, then a layer of granulated calcium chloride, and finally a thick wad of cotton-wool. To this tube is fitted a hard glass tube, drawn out into a thin tube of such external diameter that at the place where the arsenic mirror is expected the tube just passes through a No. 13 Birmingham wire-gauge (=0·092 in.). A good Bunsen flame is used to heat the wider part of the hard glass tube close to the constriction. About 1 in. of tube, including the shoulder, ought to be red-hot. A piece of moderately fine copper gauze (about 1 in. square), wrapped round the portion of the tube to be heated, assists in insuring an equal distribution of heat.

3. *Mode of Testing.*—About 20 g. of zinc are placed in the bottle and washed with water to clean the surface; all parts of the apparatus are connected and sufficient acid is allowed to

flow from the funnel so as to cause a fairly brisk evolution of hydrogen. When the hydrogen flame (which during the heating of the tube should be kept as uniformly as possible a ¼ in. high) burns with a round (not pointed) top, all air has been removed from the apparatus. The Bunsen burner should then be placed under the hard glass tube, as described, and more acid (10 to 20 c.c.) run in as required. With good materials no trace of a mirror is obtained within half an hour. Great care must be taken that, when additions of acid are made to the zinc, no bubble of air is introduced, since in presence of air the arsenic mirror may become black and uneven, whilst it should be brown.

Should the blank experiment not be satisfactory, it must be ascertained, by changing the materials methodically, whether the fault lies with the acid, the zinc, or the apparatus.

4. *Preparation of Standard Mirrors.*—A hydrochloric-acid solution of arsenious oxide, containing 0·001 mg. As_4O_6 per cubic centimetre, is prepared by diluting a stronger solution with distilled water. Two c.c. of this solution are introduced into the apparatus. If the zinc is "sensitive," a distinct brown mirror is obtained within twenty minutes. (Some "pure" zinc is, from a cause at present unknown, not sensitive.) The portion of the tube containing the arsenic should be sealed off while still filled with hydrogen. Mirrors are similarly made with 0·004, 0·006, 0·008, and 0·01 mg. of arsenious oxides. The first stage of every test must be blank for at least twenty minutes.

Arsenic in both states of oxidation can be detected and estimated by the procedure described.

The proof that the mirrors are arsenical is obtained as follows:—The narrow portion of the tube containing the mirror is cut off, the hydrogen replaced by air, and the ends sealed up. The tube is then repeatedly drawn through a Bunsen flame until the mirror has disappeared. On cooling, minute sparkling crystals of arsenious oxide deposit, which can be readily identified under the microscope. With this test quantities of 20 c.c. will give an indication in the presence of 0·000015 per cent., or 1 part arsenious oxide in 7,000,000.

I have thought it right to quote this method; but (as is the case with some which follow) it is really *too* delicate for the purposes of the acid-maker, from whom it cannot be demanded that his "purified" acid should contain less than 1 part As_4O_6 in 200,000 of sulphuric acid. It is acknowledged on most sides that acid containing such a minimum of arsenic can be employed even for the purpose of manufacturing glucose, tartaric acid, and other substances intended for human consumption.

Bertrand (*Bull. Soc. Chim.* [3] xxvii. No. 16; *Chem. News*, lxxxvi. p. 191) concentrates the arsenic in not more than 30 to 60 c.c. of liquid in the hydrogen apparatus. The oxygen is entirely driven out of the apparatus, after putting in the zinc, by pure CO_2 taken from a bottle of liquid CO_2; this takes only a few minutes Then one or two drops of dilute platinum chloride in 10 c.c. of dilute sulphuric acid (1 : 5) is added, and after ten minutes the arsenical solution is introduced. The gas is dried by cotton-wool, previously heated to 120° C. It is passed through perfectly clean glass tubes, which are chosen all the narrower the smaller the quantity of arsenic expected; *e.g.*, only 1 mm. wide, if less than $\frac{1}{300}$ mg. is present. The end is drawn out very fine for several centimetres, about 10 or 15 cms. from the place where the ring is to be formed. A space of about 20 cms. length of this tube is heated to nascent redness. If the tube is thin, nothing else need be done; if it is of thick glass, a space of the above length should be confined on both sides by a band of filtering-paper kept moist, so as to prevent the ring from spreading too fast. In this way one-thousandth of a milligram or even less can be detected; but of course the greatest care must be taken not to introduce it by the reagents. Such exceedingly slight mirrors must be kept from oxidising by sealing the tube while filled with hydrogen.

Parsons and Stewart (*J. Amer. Chem. Soc.*, 1902, xxiv., p. 1005) show that in the presence of iron some arsenic is retained in the Marsh-Berzelius flask, and hence iron should be avoided if quantitative results are required.

For the Reinsch test very detailed prescriptions are given by A. H. Allen, in *J. Soc. Chem. Ind.*, 1901, p. 281, and by the Manchester Brewers' Association, *ibid.*, p. 646; but these also refer to beer, glucose, etc.

A third test, proposed by Gutzeit, is frequently preferred on account of its simplicity. It consists in allowing hydrogen, containing arsenic, cooled as in the Marsh test, to act upon solid silver nitrate, deposited by drying on a piece of blotting-paper. Convenient forms of apparatus for this test have been constructed by Kirkby (*J. Soc. Chem. Ind.*, 1901, p. 281), by Tyrer (*ibid.*, p. 281), and by Dowzard (*ibid.*, 1900, p. 1145). *Cf.* also Hehner (*ibid.*, 1901, p. 194), Bird (*ibid.*, 1901, p. 390), Richardson (*ibid.*, 1902, p. 902), and Gotthelf (*ibid.*, 1903, p. 191).

For sulphuric acid specially Bettendorf's test is also employed, in which a solution of stannous chloride in its own weight of strong hydrochloric acid is added to the solution to be tested. In the presence of arsenic a brown colour and, later on, a black precipitate are formed much more quickly when heating. According to Messel (*J. Soc. Chem. Ind.*, 1901, p. 192) 0·01 mg. AS_4O_6 can be detected in 1 c.c. sulphuric acid by this test.

The detection of arsenic has been most thoroughly treated in a Report of a Committee appointed by the Commissioners of Inland Revenue, of which Professor T. E. Thorpe was Chairman. They recommend, in the first instance, Bloxam's electrolytic method for the reduction of the arsenic to arseniuretted hydrogen, which has been worked out in the Government Laboratory. The apparatus serving for this is illustrated and minutely described in the Report. It is somewhat costly, and of course only applicable where an electric current of sufficient intensity is available. Therefore in many cases the zinc method will be preferred, in spite of its drawbacks. This latter method, as described in the Report, agrees in most respects with the prescriptions laid down by the Arsenic Committee of the Society of Chemical Industry (*supra*, p. 370); the deviations comprise only some certainly not unimportant details. The size of the apparatus employed and the amount of zinc and acid are much smaller, the rate of evolution of the gas is less, and the arsenic is depressed over a smaller area of glass (*J. Chem. Soc.*, vol. lxxxiii., p. 974; *J. Soc. Chem. Ind.*, 1903, p. 965).

Further impurities of sulphuric acid. Hydrochloric acid (from the common salt present in the nitrate of soda) can be proved by nitrate of silver, after having diluted the acid, silver sulphate being also very little soluble; *hydrofluoric acid* is found by heating in a platinum dish covered by a glass plate coated with wax and containing scratched-in figures; *sulphurous acid* is found by the decolorisation of a weakly blue solution of iodised starch, or very accurately by reduction with zinc or aluminium to sulphuretted hydrogen, which is recognised by its turning lead-paper brown or by colouring purple an alkaline solution of sodium nitroprusside (*cf.* pp. 274 *et seq.*).

The *oxygen compounds of nitrogen* are nearly always present in the sulphuric acid of trade. They are recognised in the simplest manner, and with nearly as much precision as by any other test, either by the decolorisation of a drop of dilute solution of indigo on heating, or by carefully pouring a solution of ferrous sulphate on the acid contained in a test-tube, so that the liquids do not get mixed. In the presence of traces of nitrous acid or of higher nitrogen oxides a brown ring will be formed at the point of contact; if more be present, the iron solution is coloured brown or black; but after some time it loses colour again, especially if it has become warm by the reaction. Selenium also gives a red ring similar to that produced by traces of nitrogen oxides; but the colour, instead of gradually vanishing, after standing for some time turns into a red precipitate at the bottom of the test-tube. Nitrous and hyponitric acids are also recognised by turning blue a solution of starch containing potassium iodide.

The most sensitive reagent for nitrogen acids is *diphenylamine*, which is most conveniently employed as a solution of 0·5 g. in 100 c.c. concentrated sulphuric acid, diluted with about 20 c.c. of water. A few cubic centimetres of this solution is poured into a test-tube or conical glass, and the solution to be tested is carefully poured over it, so that the liquids mix only gradually. If traces of nitrogen acids are present, a fine blue colour is produced at the point of contact. But as all other oxidising substances, also selenious acid, produce the same blue colour, errors may occur through the (very frequent) presence of selenium, which gives the blue reaction with diphenylamine even in the absence of any trace of nitrogen acids. It is therefore necessary to test first with ferrous sulphate, as described above.

As I have shown in *Z. angew. Chem.*, 1894, p. 345, the diphenylamine reaction is best employed in the following manner: 0·5 g. white diphenylamine is dissolved in 100 c.c. pure strong sulphuric acid, adding 20 c.c. water; the heat assists in dissolving the substance, and the reagent keeps in well-stoppered bottles a long time without turning brown. When testing for nitrogen acids, pour a few cubic centimetres of the specifically heavier liquid into a test-tube and carefully pour the specifically lighter liquid on the top, so that the layers only gradually mix. The presence of as little as $\frac{1}{20}$ mg. nitrogen in the shape of nitrogen acids per litre is indicated by a blue ring forming at the surface of contact of both liquids, most easily perceived by holding the glass sideways against a white background. Both nitric and nitrous acid are indicated in this way.

Withers and Ray (*J. Amer. Chem. Soc.*, 1911, p. 708) describe the test just in the same manner; according to them, the blue ring appears in the presence of $\frac{1}{27}$ millionth of nitrous nitrogen or $\frac{1}{35}$ millionth nitric nitrogen, and when heating for an hour even with $\frac{1}{32}$ millionth nitrous or $\frac{1}{11}$ nitric nitrogen.

Brucine indicates only nitric acid if there is a great excess of strong sulphuric acid present; neither selenium nor nitrous acid interfere with this test, but nitrous acid equally reacts with brucine if there is but little sulphuric acid and much water present, say 1 : 2. In order to detect nitric acid by itself, an aqueous solution to be tested should contain at least $\frac{2}{3}$ of its volume of strong sulphuric acid. The brucine can be added either as powder or dissolved in pure strong sulphuric acid, say 1 c.c. of a solution of 0·2 g. brucine in 100 c.c. strong acid, for 50 c.c. of the solution to be tested, of which $\frac{3}{4}$ must consist of strong sulphuric acid. If as little as $\frac{1}{100}$ mg. nitric nitrogen be present, a pink colour is produced which gradually, on heating very quickly, passes through orange into yellow. In *Z. angew. Chem.*, 1894, p. 347, I have shown how this test can be utilised for a quantitative colorimetric estimation of small quantities of nitric acid. *Cf.* also *ibid.*, 1902, pp. 1, 170, and 241.

Most reagents, like diphenylamine, ferrous sulphate, and indigo, indicate both nitric and nitrous acid. There are other reagents which prove the presence of *nitrous acid* (or nitrites) *alone*, not that of nitric acid: for instance, a mixture of starch solution with a solution of iodide of zinc (a blue colour being produced), and of various organic amines, which with nitrous acid form corresponding azo-colours (Griess, *Berl. Ber.*, xi., p. 624). Of these the most frequently used are: metaphenylene diamine, which produces a yellow colour with 0·1 mg. nitrous acid in a litre, or else a combination of sulphanilic acid and α-naphthylamine (reagent of Griess). I have shown (*Z. angew. Chem.*, 1889, p. 666) that it is best to mix both substances, dissolved in dilute acetic acid, at once, and to keep this solution ready for use; any nitrous acid getting in from the laboratory air is thus betrayed from the outset by the reagent turning pink. This colour can be removed by shaking up with zinc dust and filtering. For actual use, the solution to be tested for nitrous acid is heated up to about 80° C., and a few cubic centimetres of the mixed reagent added to it, when a rose colour will be developed with less than $\frac{1}{1000}$ mg. N_2O_3 in one or two minutes. Solutions containing too much nitrous acid give only a yellow colour. In order to obtain a reagent which is not discoloured on keeping, a little of the α-naphthylamine is boiled with a few cubic centimetres of water, the hot solution is poured off, and only this is used, mixing it with dilute acetic acid and a dilute solution of sulphanilic acid.

If any nitrous acid present is carefully destroyed by treatment with urea, the ordinary reagents like diphenylamine, ferrous sulphate, and indigo, will indicate any nitric acid present, this not being acted upon by urea.

Selenium can be detected by the red colour imparted to a solution of ferrous sulphate, which after some little time turns into a red precipitate (not vanishing on heating like the brown colour produced by nitric oxide), or by means of sulphur dioxide. According to Jouve (*Chem. Centr.*, 1901, i., p. 1389) codein or morphine prove the presence of selenium, but only when 0·5 per cent. is present; SO_2 acts already with 0·01 per cent.; all of these act only on selenious, not upon selenic acid. Both acids, however, are proved by the red colour produced by the action of acetylene, if 0·001 per cent. Se is present. A little HCl hastens the separation of Se, which dissolves in the hot sulphuric acid with green colour.

Orlow (*Chem. Centr.*, 1901, i., p. 480) also rejects codein and prefers SO_2, especially on heating. Five parts H_2SO_4 + 10 parts water + 10 parts SO_2 solution give a red precipitate at once with 0·3 per cent. H_2SeO_3, but also with 0·03 per cent. after standing a few days or heating a few hours. Even 0·003 per cent. gives a rose-colour. Rosenheim (*ibid.*, 1901, ii., p. 234) discusses at length the influence of selenium on the ordinary tests for arsenic.

The quantitative estimation of the impurities contained in sulphuric acid is best carried out with various portions of the sample. Usually only the following are looked for. *Lead* is estimated by diluting the acid, if concentrated, with its own volume of water and twice the volume of absolute alcohol, whereby all the lead is precipitated as $PbSO_4$. *Iron* is estimated by reducing with pure zinc and titrating with potassium permanganate; not leaving out of sight its action upon SO_2, N_2O_3, etc. A very convenient colorimetric method for estimating traces of iron has been described by me in *Z. angew. Chem.*, 1896, p. 3; reprinted in my *Technical Methods of Chemical Analysis*, translated by Keane, 1908, vol. i., p. 381. *Arsenic* is estimated by reducing any arsenic acid to arsenious acid by a stream of SO_2, expelling this by CO_2, and precipitating by H_2S. The presence of lead, antimony, copper, platinum, etc., makes this process very complicated (*cf.* thereon McCay, *Amer. Chem. J.*, vii., No. 6). If the quantity of As is somewhat considerable, it can be reduced to As_2O_3 by SO_2, followed by CO_2; the liquid is then neutralised by soda, and the As_2O_3 titrated by iodine solution (Kisling, *Chem. Ind.*, 1886, p. 137). Further particulars are given in Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i., pp. 383-384.

The *volatile impurities* of sulphuric acid are estimated as follows:—

Sulphurous acid, if present in noticeable quantities, can be estimated by a solution of iodine according to Bunsen's method. The *acids of nitrogen* (nitrous, hyponitric, and nitric) cannot easily be present together with sulphurous acid in sensible quantity; but they occur in very considerable proportions in certain intermediate manufacturing products ("nitrous vitriol"); and the methods for estimating them are therefore of great importance. Also in chamber-acid and in more concentrated products there is much oftener nitrous or even nitric acid present than sulphurous acid; and in this case the estimation of even minute quantities is sometimes of importance, because they exert a very injurious action during the concentration of the acid in platinum.

Nitric oxide, as shown on p. 331, is soluble in sulphuric acid only in extremely slight quantities, inappreciable in any ordinary mode of testing. In practice, accordingly, no account need be taken of nitric oxide, especially in the case of the stronger acids, since in any case it cannot be present in sufficient quantity for estimation; and the analytical methods can only refer to the higher oxides and acids of nitrogen. Of these, again, only nitric and nitrous acid need to be taken into account. Nitrogen peroxide, N_2O_4 (formerly called hyponitric acid), when dissolved in sulphuric acid behaves exactly like a mixture of equal molecules of nitric and nitrous acid (p. 341). Nitrous acid itself does not exist in any but rather dilute sulphuric acid; in somewhat concentrated acid it exists as nitroso-sulphuric acid, $SO_2(OH)(ONO)$, *cf.* pp. 334 *et seq.*). The solution of this compound in sulphuric acid behaves, however, towards oxidising agents and in most other respects exactly like a solution of nitrous acid, which, in fact, is formed from it by dilution with water. Ordinarily in doing this, part of the NO_2H is decomposed into NO and NO_3H (p. 338), but this decomposition, which would interfere with the analysis, can be prevented by proper precautions, as we shall see later on.

First of all we must describe the methods for estimating *the total nitrogen acids*, that is, *nitrous and nitric acids together*, in which case the result can be calculated as N_2O_3, N_2O_5, NO_3H, etc. Frequently, for technical purposes, the N is calculated as NO_3Na.

Of the numerous methods proposed for this end I only mention those which are employed for technical purposes.

The method of Pelouze, modified by Fresenius and others, is only adapted for the estimation of nitric acid; it is, however, sometimes used for estimating a mixture of this and of nitrous acid, after the latter has been converted into nitric acid; for instance, by chlorine, potassium bichromate, permanganate, etc. It is founded upon the fact that free nitric acid oxidises ferrous chloride or sulphate, according to the equation:

$$6FeCl_2 + 2NO_3H + 6HCl = 6FeCl_3 + 2NO + 4H_2O$$

By means of potassium permanganate the ferrous salt, not oxidised by nitric acid, is estimated, and the quantity of the latter is calculated from that of the ferrous salt consumed.

This method is described in great detail in our first edition, vol. i., pp. 54 to 58, and second edition, vol. i., pp. 173 to 176; it is not repeated here, as the much handier nitrometer method has made it obsolete.

Another class of methods based upon the action of ferrous salts on the nitrogen acids is that first proposed by Schlœsing, and subsequently modified by many others. In this class of methods the process is carried on in such manner that all nitrous and nitric acid present is converted into nitric oxide, NO, which is then estimated in various ways—mostly by measuring its volume as a gas. This method is very much used by agricultural chemists, especially in the modification introduced by Grandeau. A table for reducing the volumes of NO to weights of N_2O_5 for various temperatures and pressures has been calculated by Baumann (*Z. angew. Chem.*, 1888, p. 662; reprinted in *J. Soc. Chem. Ind.*, 1889, p. 135). For nitrous vitriol this method is seldom used, because it is far more troublesome than the nitrometric methods to be subsequently described.

Many methods are based on the reduction of the nitrogen acids to ammonia by means of zinc, iron, or a combination of both. All the older forms of these methods have been superseded by the modification introduced by Ulsch (*Z. angew. Chem.*, 1891, p. 241; Lunge-Keane's *Technical Methods of Chemical Analysis*, I., pp. 311-315), which is extensively used for the estimation of nitrate of soda, but rarely for the nitrogen acids present in sulphuric acid.

The process which is mostly used for *the estimation of the total nitrogen acids* in sulphuric acids (as well as for that of nitrate of soda, *cf.* p. 132, of nitroglycerin, and for many analogous purposes) is the *nitrometer* method, founded upon a reaction discovered by Walter Crum (*Phil. Mag.*, 1840, xxx., p. 426). It consists in agitating the substance in question with mercury in presence of a large quantity of sulphuric acid, by which means all the nitrogen acids are converted into nitric oxide, NO, whose volume is ascertained by gasometric methods. Crum's process had been occasionally employed for the estimation of nitrates, *e.g.* by Frankland and Armstrong, and had been specially recommended for nitrous vitriol by G. E. Davis (*Chem. News*, xxxvii., p. 45). But it attracted very little attention, least of all from technical chemists, because it was cumbersome and expensive (requiring a mercury trough), and withal gave no very trustworthy results, owing to the difficulty of manipulation. I drew fresh attention to this process (*Berl. Ber.*, xi., p. 436), and made it generally accessible, both by proving its accuracy under the circumstances here mentioned, and by devising for it a special instrument, which made its manipulation extremely easy and simple. This instrument, which has since found a great variety of applications in gasometric and gas-volumetric analyses, some of which are mentioned in other parts of this work, has been called the *Nitrometer*. It is made in various shapes for various purposes; the shape which is used in testing nitrous vitriol is shown in Fig. 56.[1]

Its principal portion is a glass tube, *a*, of a little over 50 c.c. capacity, divided into tenths of a cubic centimetre. At the bottom it tapers to fit an elastic joint; at the top it ends in a funnel, *c*, communicating with the inner part of the tube by a three-way tap. Its plug has one bore, through which the measuring-tube communicates with the funnel, and another bore through which the contents of the funnel can be run off. The division of the measuring-tube *a* begins from the tap itself, and goes from the top downwards. The tube *a* hangs in a clamp, *e*, which can be instantaneously opened by a spring, so that the tube can be taken out. Another clamp, *f*, sliding on the same stand, carries a plain cylindrical glass tube, *b*, tapering below, of the same contents and about the same diameter as the measuring-tube. The lower ends of the two tubes are connected by a thick elastic tube. *b* slides up and down in its clamp with friction. In order to use the apparatus, *b* is placed so that its lower end is rather higher than the tap *d*, and, the latter being opened, mercury is poured in through *b* till it just comes up to the funnel *c*. As it flows into *a* from below, it will not allow any air-bubbles to remain in the tube. The tap *d* is now closed; *b* is lowered; and the acid to be tested is run into the funnel *c* by means of a measuring-pipette. Of course it is necessary to have an idea of the maximum quantity of NO which may be given off without expelling the mercury from the tube altogether, and the quantity of sulphuric acid must be chosen accordingly. By carefully opening the tap *d*, the acid is run into *a* without any air being allowed to enter;

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[1] Since I first published my above-quoted paper, Campbell, Davis, Dupont, and others have made known apparatus very similar to mine, for which they have adopted my name, *Nitrometer*. Not one of these, however, combines all the advantages found in the instrument constructed by me.

in a similar way the funnel *c* is washed out twice by means of pure concentrated sulphuric acid. It is not advisable to put

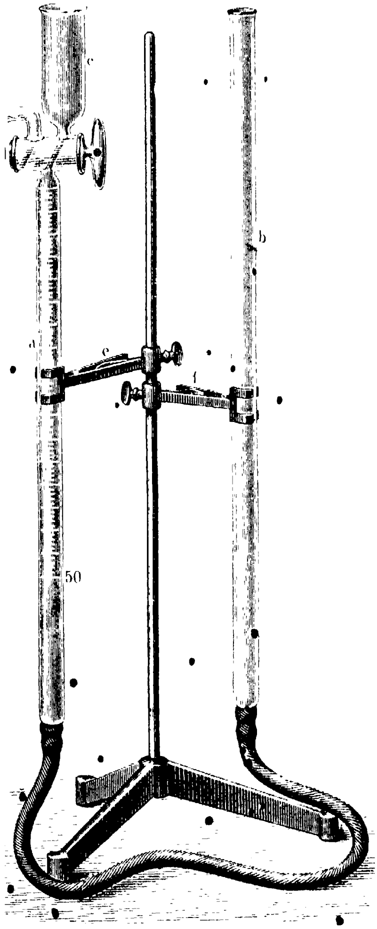

FIG. 56.

more than 8 to 10 c.c. of acid into the apparatus; much better only 4 to 5 c.c. altogether are used; but in any case there must be an excess of strong sulphuric acid present. Now the tube *a* is taken out of the spring clamp and well shaken up. The evolution of gas in the case of nitrous acid commences at once—the acid taking a purple colour, in the case of nitric acid, after a minute or so. The reaction is ended by violent shaking for one or two minutes. Sometimes it takes a long while before the acid clears and the froth subsides, but generally this is effected in a very short time; anyhow it is necessary to wait a little, so that the apparatus may assume the temperature of the air. Now by sliding *b* up or down, the level of the mercury in this tube is so placed that it is as much higher than that of *a* as corresponds to the vitriol; say, for each 7 mm. of acid 1 mm. of mercury; or else the level of the mercury is made the same in both tubes, and the height of mercury corresponding to the layer of vitriol in the tube is deducted from the barometrical pressure. In the former case, it is easy to ascertain after reading off whether the proper compensation for the height of the acid column has been made or not. It is only necessary to cautiously open the tap *d*, over which a drop of acid has been left standing. If this is sucked in, and the level of the acid falls, there has been too little pressure, and *vice versâ*. The volume of the nitric oxide can be read off to $\frac{1}{20}$ c.c.; it is reduced to 0° and 760 mm. mercurial pressure, and the percentage of the acid calculated from it. Each cubic centimetre of NO, measured at 0° and 760 mm., corresponds to 1·3402 mg. NO, or 1·6975 mg. N_2O_3, or 2·8144 mg. HNO_3, or 4·5176 mg. NO_3K, or 3·7986 mg. NO_3Na.[1] By this process, of course, nitric and nitrous acids cannot be distinguished, but are always estimated together.

After reading off, *b* is again placed higher, the tap *d* is opened so that tube *a* communicates with the small outlet tube, and thus first the nitric oxide and then the sulphuric acid, muddy with mercuric sulphate, is driven out. When the mercury begins to run out as well, the tap is closed, and everything is again ready for a new test. If any sensible quantities of sulphurous acid are present in the acid to be tested (as proved by the smell), it is best to add a very little powdered potassium permanganate to the sulphuric acid, avoiding any considerable excess.

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[1] Multiples of these figures from 2 to 9 are given in my *Technical Chemists' Handbook*, 1910, p. 17.

The nitrometer was first provided with a three-way tap on Cl. Winkler's principle, with one transverse and one longitudinal bore; but now another arrangement, known as the "Greiner-Friedrichs" or the "Geissler-Miescher" tap, and shown in the diagram, is preferred, which admits of much easier manipulation and is far less liable to leakage.

It has been stated by T. Bayley that it is necessary to dilute the acid contained in the nitrometer at the close of the experiment, in order to expel the nitric oxide dissolved by the sulphuric acid. But for ordinary purposes there is no appreciable error caused by the solubility of NO in sulphuric acid, as I showed in *J. Soc. Chem. Ind.*, 1885, p. 447, and 1886, p. 82. This could not be contradicted by Mr Bayley, who, however, contended that the iron contained in the acid as ferrous sulphate acted as solvent for NO. I replied to this (*Chem. News*, 1886, liii. p. 289) that the quantity of iron found in any commercial acid would never lead to any appreciable error of this kind, more particularly as it would be present as ferric sulphate.

For very exact purposes the solubility of NO in strong sulphuric acid, which amounts to 0·35 c.c. NO in 100 c.c. acid, must be taken into consideration. Nor must the acid employed be stronger than 94 to 94·5° per cent., to avoid the reduction of NO to N_2O or N.

In spite of the very great convenience, speed, and accuracy of the nitrometric estimation of the nitrogen acids, many chemists might have abstained from using it, because the unavoidable reduction of the volume of NO to 0° C. and 760 mm. pressure appeared too tedious to them. In order to overcome this objection, I have calculated tables which admit of reducing any volume of gas from 1 to 100 from any given temperature to 0° C., and from any given pressure to 760 mm., by simple reading off. These tables were given in the Appendix to my first edition; they are also contained in Lunge's *Technical Chemists' Handbook* (1910), pp. 138 *et seq.*, and are also separately published for use as wall-tables by F. Vieweg & Sohn, Brunswick. Other tables, requiring very little more time for use, are found in Winkler-Lunge's *Handbook of Gas-Analysis*, 2nd edition, pp. 177 *et seq.*

I abstain here from giving these or any other tables, as an instrument invented by myself, and called the *gas-volumeter*

(*Z. angew. Chem.*, 1890, p. 139; *Berl. Ber.*, 1890, p. 440), has made unnecessary all calculations and tables in connection with the reduction of volumes of gases to 0° and 760 mm. This instrument, as shown in Fig. 57, consists of three glass

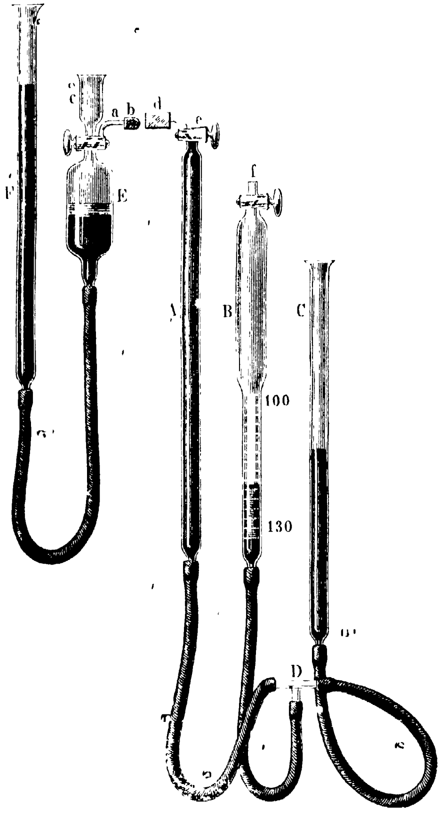

FIG. 57.

tubes, all joined by very strong elastic tubes to a three-way pipe, D, and sliding upwards or downwards in strong clips. Tube A is the measuring-tube, B the reduction-tube, C the level-tube. A is divided into tenths of a cubic centimetre, and generally holds 50 c.c.; where large volumes of gases are to be measured it is shaped like B, and holds 60 or 100 c.c. in the upper, wider portion, and another 40 c.c. (divided into $\frac{1}{10}$ c.c.) in the lower, narrower portion. The "reduction-tube" B holds 100 c.c. in the upper part, and another 30 c.c. (divided into $\frac{1}{10}$ c.c.) in the lower part. This tube is set once for all in the following way:—After putting the apparatus together and partly filling it with mercury, the temperature close to B and the barometric pressure are taken, and it is calculated, by the well-known formula

$$\frac{(273+t)760}{273 \times b}$$

(where t denotes the temperature in ° C., b the height of the barometer in millimetres), what would be the volume of 100 c.c. dry air under the existing atmospheric conditions. (This calculation can be abridged by using any of the above-mentioned tables, if they are at hand.) Suppose $t = 20°$, $b = 750$ mm. In this case 100 c.c. of dry air would occupy the volume 108·8 c.c. We now move B and C so that, tap f being open, the level of the mercury in B is at 108·8, whilst the mercury in C is, of course, at the same level. Previously to this we have introduced a drop of strong sulphuric acid into B, but not sufficient to reach over the meniscus of the quicksilver, which would be an impediment to taking the readings; this is done because gases have afterwards to be measured in the *dry* state. (In the more frequent case in which this instrument is employed for measuring *moist* gases, in lieu of sulphuric acid, a drop of water is introduced into B, and the calculation is made by deducting from the barometric pressure the tension of aqueous vapour corresponding to the existing temperature.) Now tap f is closed, and is secured so that no air can enter or escape through it. In lieu of this tap a capillary tube may be provided which is sealed by a small flame, after having put a perforated piece of asbestos cardboard over the top of tube B, to prevent its temperature rising during the sealing-operation. The best way of closing tube B is by means of a mercury-sealed tap, as described by me in *Berl. Ber.*, 1892, p. 3158.

It is quite evident that every time level-tube C is raised so that the mercury in B rises to the point 100, the air within B is compressed to the volume it would occupy at 0° and 760 mm. independent of the temperature and barometric pressure actually existing. Now suppose we have evolved or carried over into tube A a certain volume of gas, and we adjust the position of the three tubes so that the mercury in B stands at 100°, and that in A exactly at the same level, it is evident that the gas in A is under the same pressure as in B; and, supposing its temperature to be the same (which will be the case if the two tubes are close together), the gas in A will be equally compressed as that in B to the volume it would occupy at 0° and 760 mm. barometric pressure. The reading taken in A thus yields at once the corrected volume without having to look at a thermometer or barometer, or to use any calculations or tables.

Tube A might be an ordinary nitrometer; but it is far preferable to use it only as a measuring-tube, and thus to keep it always clean and dry, whilst the nitrometric operation proper is carried out in the auxiliary "agitating-vessel" E. This is a non-graduated vessel, holding 100 to 150 c.c., and connected by a strong elastic tube with the level-tube F. The vessel E bears at the top the usual three-way tap and cup *c*. The side-tube *a* can be closed by a small ground-on cap, *b*, or else by an india-rubber cap. Before commencing the analytical operation, the tube F is raised so that the mercury just issues out of *a*; cap *b* is now put on and tap *c* is closed. Now the nitrous vitriol (or solution of nitrate of soda, *cf.* p. 132) is introduced through *c*, by carefully lowering F, so that only the liquid, but no air, enters into E; strong sulphuric acid follows, to rinse out cup *c*; the tap is now entirely closed, and E is violently shaken till the decomposition is complete and no more NO is given off. The cap *b* prevents the mercury in tube *a* from being thrown out in the shaking. The instrument is allowed to cool down, and is then put in the position shown in the diagram, so that the small tubes *a* and *d* are on the same level. Previously a short piece of india-rubber tube has been slipped over *d*, and by raising C the mercury has been forced right to the end of *d*. Now cap *b* is taken off, and *a* is introduced into the short elastic tube, till the glass tubes *a* and *d* touch. Now tube C is lowered and F raised (as shown in the diagram), and tap *c* is cautiously opened (*e* having been left open before). The gas will thus be transferred from E into A; at the moment when the sulphuric acid has entered into the bore of *e*, but before it has got inside of A, tap *e* is closed. Now the reading is taken as described above; the apparatus EF may be detached at any time and cleaned as occasion requires.

The readings of the volume of NO taken in tube A may be converted into grammes of N_2O_3 or $NaNO_3$, etc., by means of the table mentioned on p. 383. If nitrate of soda has to be analysed, each cubic centimetre will indicate 3·7986 mg. $NaNO_3$; hence, if 0·3799 g. of nitrate were employed for the test, the number of cubic centimetres of NO would at once indicate the percentage of $NaNO_3$. In the case of nitrous vitriol the quantity will usually not be weighed, but measured by means of a pipette, and the results obtained must then be divided by the specific gravity of the acid, to reduce them to weight percentage. If the acid is near 140° Tw., this is unnecessary; for in this case a 1 c.c. pipette will deliver 1·70 g. acid, and as each cubic centimetre of NO indicates 0·0017 N_2O_3, this means that the number of cubic centimetres read off is exactly = tenths of a per cent. of N_2O_3 by weight of the nitrous vitriol.

We now proceed to the estimation of *nitrous acid*, or, more properly speaking, of *nitroso-sulphuric acid*, present in sulphuric acid, which is mostly sufficient for testing the "nitrous vitriol" from the Gay-Lussac tower.

Among all the analytical methods founded upon the oxidation of nitrous acid, both the most convenient and the most accurate is that employing *potassium permanganate*, first proposed by Feldhaus. Even for scientific purposes we do not possess a more accurate method for estimating nitrous acid in an acid solution than this, if other oxidisable bodies be absent.

Even nitric oxide is oxidised by this reagent, according to this equation:

$$10NO + 6MnO_4K + 9SO_4H_2 = 10NO_3H + 3SO_4K_2 + 6SO_4Mn + 4H_2O.$$

Accordingly the seminormal solution of permanganate, each cubic centimetre of which corresponds to 0·004 g. O, will show 0·005 g. NO for each cubic centimetre. Thus, on the one hand, nitric oxide can be estimated quantitatively by this reagent: on the other hand, the nitric oxide would make the estimation of nitrous acid inaccurate if it were present at the same time, which, fortunately, is not the case in sulphuric acid to an appreciable extent.

Nitrous acid itself is oxidised by permanganate, according to the equation :

$$5N_2O_3 + 4Mn_4K + 6SO_4H_2 = 10NO_3H + 2SO_4K_2 + 4SO_4Mn + H_2O.$$

Here every cubic centimetre of seminormal permanganate solution corresponds to 0·009502 g. N_2O_3.

The process formerly in use, where the permanganate solution was run into the nitrous vitriol, has been shown to be quite inaccurate by my investigations (owing to the formation of NO and HNO_3) and has been replaced by the plan proposed by myself, namely, manipulating in the following way :—The permanganate is not run into the acid, but, on the contrary, a certain volume of permanganate solution is taken, and the nitrous vitriol is run in from a burette slowly, and with constant shaking, till the liquid is just decolorised. In the cold this takes some time, since the very dilute solution of permanganate is no longer acted upon instantaneously. This loss of time can be avoided by working at 30° to 40° C., but *no higher*. When working with concentrated sulphuric acid, this temperature is attained without any special means; otherwise the permanganate solution is heated up beforehand. If seminormal solution is employed, it is diluted with about 100 c.c. of tepid water. Sometimes a brown precipitate (of hydrated manganese peroxide) is formed in the operation; but this dissolves later on, and the final result is quite as correct in these as in any other cases.

In testing chamber acid, at most 5 c.c. of seminormal permanganate should be employed; otherwise, the quantity of sulphuric acid required for decolorising it will be inconveniently large. For proper "nitrous vitriol" from the Gay-Lussac tower up to 50 c.c. permanganate may be taken. If the number of cubic centimetres of permanganate is called x, and that of the acid required for decolorising it y, the quantity of N_2O_3 present in grammes per litre of acid is $\frac{9{\cdot}502\,x}{y}$ calculated as

$$NO_3H = \frac{15{\cdot}75\,x}{y},$$

or as

$$NaNO_3 = \frac{21.258\,x}{y}$$

A table given in my *Technical Chemists' Handbook*, 1910, p. 137, saves the calculation in all cases in which $x = 50$.

In the presence of *other oxidisable substances*, such as sulphurous acid, ferrous salts, organic substances, etc., all oxidation methods are of course inexact—whether the bleaching-powder, or the bichromate, or the permanganate process. Generally those impurities are too insignificant to do any harm; but, especially where large quantities of nitrous acid are present, as in the nitrous vitriol from the Gay-Lussac towers, the permanganate process is quite sufficient for the purpose of checking the course of manufacture. Of the oxidisable substances only arsenious acid sometimes occurs in sufficient quantities to affect the results sensibly, but to a small extent only, in nitrous vitriol, where it is mostly changed into arsenic acid.

The estimation of nitrous acid by means of *aniline*, which is converted into a diazobenzol salt, the end of the reaction being shown by potassium iodide and starch, has been practised for some time at several colour-works, long before it was published by Green and Rideal (*J. Soc. Chem. Ind.*, 1886, p 633). According to comparative tests made in my laboratory, it offers no advantage whatever over the very much less troublesome permanganate method, and may lead to serious errors (*Z. angew. Chem.*, 1891, p. 629; 1902, p. 169).

Minute quantities of nitrogen acids cannot be quantitatively estimated by the above methods, but the *colorimetric estimation of slight quantities of nitrous acid*, as I have shown in *Z. angew. Chem.*, 1894, p. 348, can be performed by Griess's reagent, modified as follows:—0·1 g. white α-naphthylamine is dissolved by boiling in 100 c.c. water for a quarter of an hour; then 5 c.c. glacial acetic acid (or its equivalent in ordinary acetic acid) and a solution of 1 g. sulphanilic acid in 100 c.c. water are added. The solution is kept in a well-stoppered bottle; if it turns pink it is decolorised by shaking with zinc-dust and filtering. A very slight colour does not interfere with its use, as only 1 c.c. is employed for 50 c.c of the solution to be tested. One c.c. of the reagent indicates $\frac{1}{1000}$ mg. nitrous nitrogen in 100 c.c. water by turning the water pink in ten minutes. Strong mineral acids retard or stop the reaction, but this can be remedied by adding a large excess of pure sodium acetate.

For quantitative use a standard solution is prepared as follows:—0·0493 g. pure sodium nitrite, containing 0·010 g. nitrogen, is dissolved in 100 c.c. water, and 10 c.c. of this solution is drop by drop added to 90 c.c. pure sulphuric acid; the resulting mixture contains $\frac{1}{100}$ mg. of nitrous nitrogen in a perfectly stable form. Two colorimeter cylinders are charged as follows:—Each of them receives 1 c.c. of the Griess-Lunge reagent, 40 c.c. of water, and about 5 g. of solid sodium acetate. To one of these is added 1 c.c. of the standard solution, to the other 1 c.c. of the acid to be tested. The contents of each cylinder are at once thoroughly mixed, and after five or ten minutes the colours are compared. If they do not correspond, the more strongly coloured liquid is diluted up to the point where layers of equal thickness show the same depth of colour in both solutions, and the percentage of nitrous nitrogen is calculated from the amount of dilution.

Very minute quantities of *nitric acid* are best estimated by the *colorimetric brucine process*, described by me, *Z. angew. Chem.*, 1894, p. 347, the principle of which consists of comparing the yellow colour obtained by heating to about 70° with brucine with a standard solution of nitric acid. As a rule, nitric acid is not estimated by itself in sulphuric acid, but indirectly, by estimating the total nitrogen acids by means of the nitrometer (p. 380) and deducting the nitrous acid found by the permanganate method (p. 387).

Finch (*Z. Schiess und Sprengwesen*, 1912, pp. 113 *et seq.*) discusses the volumetric methods for estimating sulphuric, nitric, and nitrous acid in mixed acids for nitrating purposes, and in the waste acids produced in those operations.

CHAPTER II

THE RAW MATERIALS OF THE SULPHURIC-ACID MANUFACTURE (INCLUDING NITRIC ACID)

1. NATURAL SULPHUR (BRIMSTONE).

BRIMSTONE, owing to its being found in nature in the free state, has been known to mankind since very ancient times. It is hardly necessary to point to its being noticed in the Bible; it is also mentioned several times in the Homeric poems. The Romans evidently obtained it in the same way as is done now, by melting it out of its mixture with marl, etc. The ancients employed it principally for fumigating purposes, both on account of its disinfecting properties and as a religious rite (compare the well-known passage from the Odyssey, where Ulysses purifies his house after slaying the intruders), but also for many of the uses to which it is put at the present day, as for cleaning wine-casks, for destroying fungus-growths in vineyards and orchards, for plasters in skin diseases, for lighting fires and preparing torches, for cementing glass, for bleaching, for "niello" work on metals.[1]

In modern times brimstone has been used for most of the just-mentioned purposes and for many others; but we are here concerned only with its use for the manufacture of sulphuric acid. Brimstone is undoubtedly the most convenient raw material for this manufacture, and for a long time all the sulphuric acid of commerce, apart from Nordhausen acid, was made from it; but its use in this respect has been almost entirely abandoned in most countries, and is not likely to be revived there, since iron-pyrites, and more especially that containing a few per cent. of copper, and zincblende supply sulphur for the above purpose, far more cheaply than natural brimstone ever can do. In spite of this, brimstone is still a principal raw material for the manufacture of sulphuric acid in America (where, however, it has lost its former exclusive sway), and it is also used to some considerable extent in England for that purpose, but very little indeed in other European countries.

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[1] I owe these historical notes to a treatise by Professor Blumner, of Zürich, in the *Festschrift zur Begrussung der Philologen-Versammlung* (Zurich, 1887), pp. 23 *et seq.*

As late as 1902 a large brimstone acid factory was erected in Ireland without a Gay-Lussac tower (*Alkali Inspector's Report*, No. 38, p. 50).

According to Quincke (*Z. angew. Chem.*, 1909, p. 2029) it cannot be said that recently brimstone has been more than formerly used for the production of sulphuric acid; the production of Louisiana sulphur (see below) is not increasing, and in Sicily the sale of sulphur is meeting with difficulties.

A somewhat considerable quantity of brimstone is also consumed in the manufacture of sulphurous acid, principally in order to prepare bisulphite of lime for the manufacture of wood-pulp.

Sulphur is an element whose atomic weight is now assumed to be 32·07 (oxygen = 16). It is very brittle; its hardness is from 1·5 to 2·5 of the ordinary mineralogical scale; its specific gravity is 2·07. As usually occurring, it is semi-transparent at the edges and of the well-known bright yellow colour; at $-50°$ it is nearly devoid of colour. Its taste and smell are very slight. It does not conduct electricity, but itself becomes electric by friction; and it is therefore difficult to powder it finely, as it adheres to the mortar and pestle.

Sulphur melts at 111°·5 C., and forms a thin, light-yellow liquid, which, on being more strongly heated, becomes darker and thicker; at 250° to 260° C. it is nearly black, and so viscid that it does not run out when the vessel is upset; at a still higher temperature it becomes thinner again, keeping its brown colour and emitting brownish-red vapours.

Sulphur slightly volatilises already at ordinary temperatures, as evidenced by its blackening silver in contact with it (which by some, however, is attributed to the formation of H_2S). Moss (*Abstr. Chem. Soc.*, 1907, ii. p. 20) kept ordinary roll sulphur sealed up in an exhausted tube; after twenty years, during which time the tube was kept in a horizontal position, a crystalline sublimate was observed. Porter (*Proc. Chem. Soc.*, 1898, p. 65) and Dewar (*Proc. Roy. Soc.*, 1865, p. 7) had made similar observations. The vapour pressures of sulphur at temperatures below its boiling-point have been studied by Matthies (*Phys. Zsch.*, vii. p. 395); H. Gruener (*Science*, 1905, p. 74; *Z. angew. Chem.*, 1905, p. 1907); later on by the same chemist in *J. Amer. Chem. Soc.*, 1907, pp. 1396-1402; *Z. anorg. Chem.*, lvi. pp. 145-152); Ruff and Graf (*Berl. Ber.*, 1907, pp. 4199-4205). According to the last-mentioned chemists the vapour pressure of sulphur is 0·002 mm. at 78°; 0·01 mm. at 104°; 0·1 mm. at 135°; 1 mm. at 181°; and 10 mm. at 245°.

The boiling-point of sulphur at ordinary pressures is stated by Holborn and Grüneisen (Drude's *Ann.*, 1901, vi. p. 123) = 444·8°; by Callendar (*Proc. Roy. Soc.*, 1908, p. 329) = 443·58°.

Modifications (Allotropic Conditions) of Sulphur.—Sulphur exists in different allotropic conditions. The α-modification forms rhombic crystals, mostly pointed rhombic octahedra, whose physical properties have been described above; this α-modification is that of which the brimstone found in nature consists, and it is also obtained by crystallising sulphur from its solution in carbon disulphide. Its specific gravity is = 2·07. The β-modification is obtained by slowly cooling melted sulphur, and pouring off the liquid portion when another portion has crystallised; it consists of long thin oblique rhombic prisms, belonging to the monoclinohedric system, of a brownish-yellow colour, transparent, sp. gr. 1·982; they gradually pass over into the α-modification, completely so after a few days, even at the ordinary temperature, and suddenly by shaking or scratching. (Brauns, however, as reported in *Chem. Cbl.*, 1906, i. p. 8, kept a sample of monoclinic sulphur for two and a half years, and lost it merely by accident.) The colour then becomes light yellow; and the crystals lose their transparency, but remain as pseudomorphs of the β-sulphur. The sulphur in rolls consists, when fresh, of β-sulphur—after a short time, of α-sulphur. When sulphur has been heated up to the point of viscosity, and is then poured into very cold water, the γ-modification is formed, viz. amorphous, soft, tough, reddish-brown sulphur, of 1·957 sp. gr.; this also is gradually converted into α-sulphur; but it takes some time before this conversion is complete. The tough state lasts very much longer if resinous substances, iodine, etc., are mixed with the sulphur, even in very small quantity. This modification forms part of the "flowers" of sulphur (see below).

Extensive investigations on this modification, usually called "amorphous sulphur," have been made by Alexander Smith, Holmes and Hall (*Z. physik. Chem.*, xlii. p. 469, and lii. pp. 602-625; *J. Amer. Chem. Soc.*, 1905, pp. 797-820; *Chem. Cbl.*, 1903, i. p. 274, and 1905, ii. p. 601); Alexander Smith and Holmes (*Z. physik. Chem.*, liv. pp. 257-293; *J. Amer Chem. Soc.*, 1905, pp. 979-1013); Al. Smith and Carson (*Z. physik. Chem.*, lvii. pp. 685-717; *Abstr. Chem. Soc.*, 1907, ii. p. 208); Carson (*J. Amer. Chem. Soc.*, 1907, pp. 499-517); Al. Smith and Brownlee (*Z. physik. Chem.*, 1907, p. 209); Brownlee (*J. Amer. Chem. Soc.*, 1907, pp. 1032-1052); Smith and Carson (*Z. physik. Chem.*, xi. p. 661; *Abstr. Amer. Chem. Soc.*, 1911, ii. p. 977).

We cannot go into details about their manifold results, and will only say that evidently several forms of this "amorphous' sulphur exist, solid, semi-solid or pasty, and liquid, and that the "soluble" or "soft sulphur," formed by precipitation from polysulphides, is not amorphous, but crystalline.

Further researches in this field have been made by W. Spring (*Naturw. Rundschau*, 1906, p. 494); Quincke (*Ann. Physik.* [4], xvi. pp. 625-711); Domergue (*J. Pharm. Chim.*, 1904, xx. p. 493), Raffo (*J. Soc. Chem. Ind.*, 1908, p. 747).

Engel (*Compt. rend.*, 1891, p. 866) found a new crystalloid modification of sulphur and another modification, soluble in water.

Sulphur sometimes appears of a *blue* colour, which has been studied by Paternò and Mazzuchelli (*Chem. Cbl.*, 1907, ii. p. 11; *Abstr. Chem. Soc.*, 1907, ii. 451).

The "dynamic allotropy" of sulphur is treated by Kruyt (*Z. physik. Chem.*, 1908, pp. 513-561); the changes in the viscosity of "liquid" sulphur by Protinjanz (*ibid.*, 1908, pp. 609-621); colloidal sulphur by Raffo (*Z. Chem. Ind. v. Colloide*, 1908, p. 358).

Solubility.—The behaviour of sulphur against water and aqueous solutions of acids and salts, in which "colloidal" sulphur is soluble to some extent, has been studied by several chemists, among whom we mention Ruff and Graf (*Berl. Ber.*, 1907, p. 4199); Raffo (*J. Soc. Chem. Ind.*, 1908, p. 747); Odén (*ibid.*, 1911, p. 941); Raffo and Mancini (*Chem. Cbl.*, 1910, ii. p. 1129; 1911, ii. p. 1305).

Under ordinary circumstances sulphur is insoluble in water, very little soluble in alcohol and in glycerin, a little more so in essential oils. The α- and β-modifications are easily soluble in carbon disulphide and in chloride of sulphur.

Physiological Action.—The action of sulphur on the fungus (Oïdium Tuckeri) which causes the grape disease is by Marcille (*Ac. des Sciences*, March 20, 1911; *Chem. Zeit.*, 1911, *Rep.*, p. 426) ascribed to the sulphurous and sulphuric acid adhering to various forms of sulphur. This explains why the action of resublimed brimstone in that respect is strongest, while the ordinary descriptions of sublimed and ground brimstone contain only 0·01-0·02 per cent. H_2SO_4 and are less efficient. Marcille therefore recommends introducing gaseous SO_2 into the condensation chambers for sulphur, intended to be employed against the Oïdium.

Demolon (*Compt. rend.*, 1912, p. 524) observed that sulphur, *e.g.* in the shape of spent oxide of iron from the purification of coal-gas, if used as a fertiliser, had a beneficial influence on the development of chlorophyll.

The action of sulphur against skin-diseases can be only alluded to here.

Combination of Sulphur with Oxygen.—On heating in the presence of oxygen or gaseous mixtures containing it (air), sulphur inflames. According to Moissan (*Comptes rend.*, cxxxvii. (1903), p. 547), solid or liquid sulphur inflames at ordinary atmospheric pressure in oxygen at 282°, in air at 363°. A mixture of sulphur vapour and air inflames already at 285°. If the air contains SO_2, the inflaming-point is much higher; with 5 per cent. SO_2 it is 445°, with 10 per cent. SO_2: 465°. The slow combination of S with O commences at a much lower temperature; it is quite sensible at 100° within twelve hours, but goes on very slowly already at ordinary temperatures.

J. Rutherford Hill (*Chem. News*, 1907, xcv. p. 169) states that in 1890 he had found the inflaming-point of sulphur at ordinary atmospheric pressure = 248°. He criticises Moissan's process and the figures found thereby as not correct.

Friedrich (*Chem. Cbl.*, 1969, ii. p. 316) found the inflaming-point of sulphur in oxygen = 270°, in air = 348°.

Kastle and M'Hargue (*Amer. Chem. J.*, 1907, xxxviii. pp. 466-475) found that when sulphur burns in oxygen at atmospheric pressure, about 2·73 per cent. is converted into

SO_3; when burning in air, about 7 per cent. of the S forms SO_3. The humidity and the presence of CO_2 has little influence on the proportion of SO_3 formed, but nitrogen acts considerably, probably as a carrier of O to SO_2, evidently being itself oxidised in the first instance.

M'Crea and Wilson (*Chem. News*, xcv. p. 169; xcvi. p. 25) found the inflaming-point of sulphur = 265°. Already far below this SO_2 is formed.

Sulphur burns with a purplish-blue flame. In forming sulphur dioxide (SO_2) it gives out 2221 metrical units of heat per gramme of sulphur. More exactly, according to Thomsen (*Berl. Ber.*, 1880, p. 959), the heat evolved in burning the different modifications of sulphur, expressed in atomic calories (that is, applied to 32 g. of sulphur), is:—

$$\text{S (rhombic, octahedric)} + O_2 = SO_2 = +71{,}080 \text{ cal.}$$
$$\text{S (monoclinic)} \;.\;.\;.\; + O_2 = SO_2 = +71{,}720 \text{ cal.}$$

Hence the conversion of 32 parts by weight of monoclinic into rhombic sulphur is accompanied by the evolution of 640 calories. Berthelot, however (*Comptes rend.*, xc. p. 1449), states the figure for octahedric sulphur = +69260 atom. cal. = 2164 g.-calories.

Hydrogen combines with sulphur very slightly at a temperature of 120°, very sensibly so at 200°. On boiling sulphur with water, hydrogen sulphide is evolved and sulphuric acid is found in the residue (Cross and Higgin, *J. Chem. Soc.*, xxxv. p. 249; *cf.* also Colson, *Bull. Soc. Chim.* [2], xxxiv. p. 66; Bohm, *Jahresber.*, 1883, p. 225).

Commercial Descriptions of Sulphur.—The sulphur occurring in commerce as *refined sulphur*, in *rolls* or as *rock-sulphur*, is frequently almost chemically pure. *Flowers of sulphur* always contains a little sulphurous acid, also some sulphuric acid, persistently retained in spite of prolonged washing; this form owes its greater efficacy against diseases of the vine (oidium) and other cases principally to this property.

O. Roessler (*Arch. Pharm.*, 1887, p. 845) states that sulphur in rolls is practically free from acids of any sort. Flowers of sulphur contain a somewhat considerable quantity of sulphurous acid (100 g. up to 3·14 c.c. of SO_2), which may be partially oxidised to sulphuric acid; thiosulphuric acid is not found in it, but in milk of sulphur (up to 0·15 per cent.).

Natural Occurrence of Sulphur.

Sulphur occurs in nature in very large quantities, both in the free state and in combination with other bodies as sulphides and sulphates. Deposits of sulphur are forming at the present day, especially in volcanic countries, by the decomposition of sulphuretted hydrogen and of sulphurous acid.

Daubrée (*Comptes rend.*, xcii. p. 101) noticed a recent formation of sulphur in the subsoil of Paris, from the action of organic substances on sulphates; and the same action has been observed in many mineral springs, where it is especially attributed to the action of Algæ, such as *Beggiatoa*, *Oscillaria*, and *Ulothrix* (*Comptes rend.*, xcv. pp. 846 and 1363).

But of far more consequence are the beds of sulphur deposited in former geological periods. The most important of all are those of *Sicily*, in the chalk. The Sicilian sulphur industry is described in detail by Angelo Barbaglia in Hofmann's Official Report on the Vienna Exhibition, i. p. 144, and by Parodi (*Ber.*, 1874, p. 358).

Further descriptions of the Sicilian sulphur industry are found in the *Chem. Zeit.* of 1882, pp. 1389, 1405, 1421; also in *Z. angew. Chem.*, 1890, p. 56, in the *J. Soc. Chem. Ind.*, 1890, p. 118; by Bechhold, *Z. angew. Chem.*, 1894, p. 33; by Frank, *ibid.*, 1900, p. 843; by Iungfleisch (*Monit. Scient.*, 1901, p. 511); in *Chem. Trade J.*, xxxv. p. 92; by Bruhn (*Chem Ind.*, 1910, p. 64).

Probably the most exhaustive description of the modern Italian sulphur industry is that given by Aichino, in *Mineral Industry*, viii. p. 592, and by Phelen, in *Min. Ress. Unit. States*, 1910, ii. p. 785.

The principal Sicilian sulphur districts are near Girgenti, Cattolica, Licata, Caltanisetta, Racalmuto, Zolfari, Committini. The sulphur region has an extension of about 100 to 500 miles from east to west, and 55 to 60 miles from north to south. The sulphur beds belong to a number of small owners, part of them being let to undertakers, and the methods of extraction are kept greatly behind by the lack of intelligence and capital caused thereby. The men work partly in the sulphur mines, and partly in their own vineyards, etc. In 1904 there were about 400 mines, large and small, of very different degrees of efficiency. The ores found there sometimes contain up to 70 per cent. sulphur; but on the average the "richest ores" contain 30 to 40 per cent., the "rich ores" 25 to 40 per cent., the "middling ores" 20 to 25 per cent. S. The first class yields 20 to 25 per cent., the second 15 to 20 per cent., the third 10 to 15 per cent. saleable sulphur. Ores below 8 per cent. S do not pay for working.

According to Frank (*loc. cit.*) the total stock of sulphur in Sicily, as far as it has been hitherto proved, is estimated at 65 million tons (former estimates speak only of 10 or 20 million tons).

The first quality of Sicilian sulphur (prima Lercara[1] or prima Licata) is of a fine amber colour, in large shining pieces, and does not contain more than 1 per cent. ash. The second quality (seconda vantaggiata) is still fine yellow, but not so shining, with ash up to 2 per cent.; the third (terza vantaggiata), which is that generally used for sulphuric-acid making, contains up to 5 per cent. ash and is coloured brown, partly by bituminous substances, partly by amorphous sulphur.

The following are analyses of Sicilian brimstone, by Mène (probably "best thirds") (*Monit. Scient.*, 1867, p. 400):—

Sulphur soluble in CS_2 .	96·2	92·1	92·1	91·3	90·1	90·0	88·7
Sulphur insoluble in CS_2 .	...	...	...	1·5	2·0	2·1	1·7
Carbonaceous matter .	0·5	1·0	1·1	0·7	1·0	1·1	1·0
Sand . . .	1·5	2·3	2·8	3·3	2·3	2·8	5·5
Limestone and strontium sulphate . . .	1·8	4·1	3·0	2·5	4·1	3·0	2·8
Total . .	100·00	99·5	99·0	99·3	99·5	99·0	99·7

The average price of sulphur in Sicily in 1881 was 115 lire; in 1882, 105 lire; in 1887 only 69 lire (say £2, 15s.) per ton.

A report by the Italian Minister of Agriculture for the year 1894 (*Chem. Ind.*, 1895, p. 182) describes the depressed state of the Sicilian sulphur industry.

In 1896, by the formation of the Anglo-Sicilian Sulphur Company, working with English capital, the Sicilian sulphur industry was at last placed on an economically sound basis, and at the same time the ruinous cutting down of prices ceased. During 1900 the average price for "best thirds" was £3, 13s. 6d. per ton f.o.b. Catania.

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[1] The Lercara mine is now exhausted (1911).

	1899-1900.	1900-1901	1901-1902	1902-1903	1904.	1905.	1906.	1907.	1908.	1909.	1910.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons	Tons.	Tons.	Tons.	Tons.	Tons.
United States and Canada . .	138,846	147,094	141,617	168,919	100,680	70,332	41,283	9,476	18,006	14,700	12,060
France	98,393	98,455	74,384	67,249	103,042	96,170	67,536	59,725	93,829	90,240	95,230
Italy (mainland)	101,624	85,210	74,517	45,603	79,619	99,683	79,519	58,926	90,551	50,180	63,200
Germany	26,290	30,549	23,447	25,906	31,613	28,319	34,967	37,100	30,399	28,540	30,230
Norway, Sweden, Denmark . .	18,213	27,373	24,485	24,918	20,120	18,288	21,608	25,155	22,609	15,540	20,210
Greece and Turkey . . .	19,795	22,304	21,701	20,548	25,376	23,069	26,560	27,608	27,812	16,310	21,090
Great Britain	25,933	19,923	22,403	25,477	18,108	18,847	20,883	16,561	20,119	19,870	19,085
Russia	16,815	19,878	15,110	17,295	15,141	16,673	16,181	15,210	29,960	21,620	25,870
Austria and Hungary . . .	23,067	19,647	18,842	19,080	23,374	23,111	22,756	24,597	32,581	26,570	29,800
Holland	11,781	15,813	10,858	8,648	8,122	4,425	5,539	11,379	8,775	11,000	9,730
Portugal	11,462	11,315	11,335	10,641	*12,436	15,674	15,422	12,778	12,894	19,620	18,760
Belgium	8,845	9,316	7,462	12,323	13,627	14,442	33,940	8,853	11,410	16,380	14,385
Spain	6,298	3,566	2,979	2,249	...	. .	...	.	...	...	...
Other countries	10,259	11,059	9,889	18,484	24,487	23,277	21,238	26,646	13,721	9,935	5,780
Total exportation . .	517,741	521,497	459,030	467,319	475,745	456,260	387,432	334,014	337,066	364,900	396,120

* The figures for Portugal include Spain from 1904 onward. The quantities for a number of years previously to the above are given in our second edition.

In the year 1906 the whole of the Sicilian brimstone producers were compelled to join the "Consortium for the Sicilian sulphur industry" for twelve years; 3·55 per cent. interest on the capital being guaranteed by the State, which nominates the general manager.

The Sicilian sulphur industry has, of course, been extremely damaged by the enormous development of the Frasch process in the United States (see below). Details on this point are given in the speech of Mr Frasch on the presentation to him of the Perkin medal, reported in *J. Chem. Soc. Ind.*, 1912, pp. 139 *et seq.*

The table on p. 20 shows the exportations of sulphur from Sicily from 30th June of one year to 30th June of the next.

The German Consulate at Palermo (*Z. angew. Chem.*, 1908, p. 1946) makes statements concerning Sicilian sulphur, to which we append some more recent statements:

Year.	Production	Exportation	Year	Production.	Exportation.
	Tons	Tons		Tons.	Tons.
1902	503,356	467,319	1907	399,672	341,951
1903	536,044	475,508	1908	413,580	375,073
1904	499,382	475,745	1909	402,354	364,901
1905	538,354	456,260	1910	395,836	395,959
1906	471,190	401,627			

In 1909, 59·70 per cent. of the Sicilian sulphur was obtained in ovens, 28·76 per cent. in calcaroni, 9·94 per cent. by superheated steam, 0·88 per cent. by other methods. Campania, in 1909, produced 40,298, Calabria 38,553, Siena 3091 tons sulphur.

The total production of sulphur in Italy (including the Romagna, etc.) has been:—

Year.	Tons.	Year.	Tons.
1901	554,096	1906	491,942
1902	530,938	1907	420,000
1903	545,030	1909	435,060
1904	519,255	1910	430,360
1905	559,967		

Oddo (*Chem. Zeit.*, 1908, p. 145) says that the percentage of sulphur in the Sicilian ores is greater than is usually stated, and in his opinion the acid made from them costs one-third less than from pyrites. He thinks the poorer ores should be used on the spot and the richer ones exported to America. [We shall see below that it is too late for such proposals.] Bruhn

(*Chem. Zeit.*, 1908, p. 457) decidedly objects to Oddo's opinion on the possibility of Sicilian ore competing with pyrites; *cf.* also *Z. angew. Chem.*, 1909, p. 560. Another paper on this subject by Oddo appeared in 1910 (*Gazz. Chim. Ital.*, 1910, pp. 217-312; abstract in *J. Soc. Chem. Ind.*, 1910, p. 624).

Northern Italy formerly yielded a very large quantity of brimstone, especially the Romagna; but many of the beds are now exhausted. The production decreased from 23,274 tons in 1886 to 21,663 tons in 1887, and 21,269 in 1901. It was 21,926 tons in 1907, 25,105 in 1908, 23,068 in 1909. The whole of this brimstone is used for inland consumption, as a remedy against the vine-disease.

Sulphur containing *selenium* is found in the Lipari Islands and near Naples, but not in quantity.

In many other parts of the world deposits of sulphur have been found, but, with exception of those discovered in the United States, they have made as yet no impression on the sulphur trade. The more important of these sulphur-mines are the following:—

The *United Kingdom* produces no native brimstone, but only sulphur recovered from alkali-waste with which we are not concerned here. According to the Annual Statement of the Trade, etc. ("Bluebook"), for 1910, the following quantities of brimstone were exported and imported, stated in cwts.:—

	1906	1907	1908.	1909	1910	1911.
Exports . .	82,445	51,889	44,932	41,877	43,627	...
Imports . .	500,650	346,854	385,442	417,509	403,438	418,700

Andalusia produces sulphur, some of which is refined in Almeria.

In *Germany* sulphur has been found at Stassfurt (*Berl. Ber.*, 1890, p. 192) and in Upper Silesia, near Ratibor, where beds up to 20 ft. thick exist (*Chem. Ind.*, ii. p. 136; *Fischer's Jahresber.*, 1882, p. 223; Gottstein, in *Chem. Zeit.*, 1907, p. 269). It has been worked by extracting it from the ore by means of carbon disulphide.

The production of sulphur in Germany, as indicated by the official statistics, does not distinguish between natural sulphur and that which is recovered in the Leblanc process. It amounted in 1897 to 2317 tons; in 1898 to 1954 tons; in 1899 to 1663 tons.

In 1899 the importation was 31,196 tons; in 1900, 40,689 tons; in 1901, 32,750 tons; in 1902, 27,186 tons; in 1909, 42,941 tons; in 1910, 46,776 tons. The exportation is insignificant. Most of the sulphur is employed there for the manufacture of "sulphate paper pulp" from wood.

In *Austria*, at Swoscowice near Cracow, an old sulphur-mine exists which for some years was carried on with great vigour, the sulphur being extracted from the marl by means of carbon disulphide. This bed is now practically exhausted, and the mine has ceased working (Wagner's *Jahresber.*, 1878, p. 333, 1879, p. 272; *Fischer's Jahresber.*, 1885, p. 204). A large deposit of native sulphur is reported to have been found in the Borgó Alps, in Transsylvania (*Chem. Ind.*, 1903, p. 147).

In *Greece*, on the island of Milo, sulphur-ore is found which is used in the raw state for dusting the vines; about 1000 tons per annum are extracted as pure brimstone.

Russia possesses considerable stores of sulphur. A bed of brimstone has been found by Gluschkoff in the Astrachan Government, on the east bank of the Baskuntschak salt-sea; it is a mixture of sandy rock with 30 to 35 per cent. of pure sulphur (*Fischer's Jahresber.*, 1884, p. 264). In West Siberia considerable beds of sulphur are said to exist. In the Vistula district a sulphur-bed is being worked at Czarki, which in 1883 yielded 60,000 pud. In the sandy steppe of Karakum a large number of conical hills have been discovered consisting of sulphury rock of 50 per cent. (*Chem. Zeit.*, 1884, p. 478). In the north of the Caucasus, in the Grodno district, sulphur has been found by Baron Heyking (*Chem. Zeit.*, 1887, p. 1630). According to *Chem. Ind.*, 1892, p. 443, sulphur is obtained at Tschirkat in Daghestan to the extent of 300,000 pud (at 40 lb.) per annum; the selling price was then 1·18 roubles per pud.

According to *Chem. Zeit.*, 1894, p. 2002, a large bed of brimstone has been found in Transcaspia, 60 versts from the port of Usun-Ada on the Caspian Sea, only 2 versts from a railway-line. The bed is just below the surface of the ground and is worked by open quarrying. The ore contains from 35 to 40 per cent. sulphur, and costs 20 to 25 copecks at Usun-Ada. If the results expected were realised, Russia would become entirely independent of Sicilian sulphur. Possibly this is the same occurrence which is reported in *J. Soc. Chem. Ind.*, 1900, p. 867, as "the richest in the world," 100 miles from Khiva, extending over 23 square miles, but nothing has been heard of it since.

In *Turkestan*, north of Aschabad, according to *Chem. Zeit.*, 1912, p. 766, the sulphur beds existing there are to be worked by a newly formed Company.

Chonski (*Chem. Zeit. Rep.*, 1895, p. 411) reports on the production of sulphur, which, he says, has been tried in several places in Russia, but has been everywhere discontinued. He enumerates the drawbacks connected with the various methods for extracting sulphur from the raw ore. This paper should be consulted by those who consider any newly discovered vein of sulphur-ore as being equal to ready money.

According to *Eng. and Min. World*, 14th October 1911, the Caucasus and Trans-Caspian beds are not worked because the Russian producers of sulphuric acid, on account of the high cost of carriage, prefer to use foreign pyrites.

Cf. on Russian brimstone, also *Z. angew. Chem.*, 1897, p. 36; *Chem. Ind.*, 1898, p. 241; Niedenführ, *Chem. Zeit.*, 1897, No. 30; Machalski, *Eng. and Min. J.*, lxx. p. 216; *Chem. Trade J.*, 1900, xxvii. p. 220.

Brimstone is got near Mossul in *Mesopotamia*, near *Cairo*, and in *Tunis*. At Djemsah and Ranga, on the coast of the *Red Sea*, the "Compagnie Soufrière" is said to get 300 tons monthly.

Very large quantities of sulphur are said to exist in *Iceland*, even more important than those in Sicily; the deposits at Guldbringe Syssel, in the south-west of Iceland, were some time ago at work with satisfactory results (*Chem. News*, xl. p. 31).

Japan possesses very large stores of sulphur, but the absence of facilities for increasing its output and for shipping it has hitherto very much restricted the development of the sulphur industry in that country. Formerly (cf. *J. Soc. Chem. Ind.*, 1890, p. 344) there was only one place where sulphur was worked on a somewhat considerable scale, namely Atosanobori, near Kushiro, on the south-east coast of the island in which the port of Hakodate is situated. The Atosanobori mine is part of an extinct volcano, whose crater and slopes are partially covered with a 50-per-cent. sulphur-ore. According to the lowest estimate this mine contains a million tons of good ore, but there is probably five times as much. The output in 1905 was about 20,000 tons per annum; the cost of the sulphur free on board at Kushiro was then about £1, 10s, 10d., but it has hitherto been shipped from Hakodate, where it cost £2, 3s. 2d. per ton in 1900, which is not remunerative. In 1905 the price was from £3, 2s. to £3, 10s., according to quality. The exportation was 1541 tons in 1885; 4972 tons in 1886; 7096 tons in 1887; 3609 tons in 1888; 15,700 tons in 1895; 14,435 tons in 1900; 10,705 tons in 1901; about 15,000 tons in 1905; 33,600 tons in 1907; 33,700 tons in 1908. The shipments generally go to San Francisco. Ordinary Japanese sulphur has a greyish colour.

Apart from the ordinary sulphur, which sometimes contains traces of selenium and tellurium, there occurs in Japan an orange-red variety, containing 0·17 per cent. Te, 0·06 Se, 0·01 As, traces of molybdenum and earthy matters (Divers and Shimidzu, *Chem. News*, 1883, No. 1256).

A considerable source of sulphur has been discovered on the volcanic island of Etrofu, about half-way between the northern extremity of Japan and Kamschatka. In 1900 already 10,000 tons sulphur were mined, and it is expected to reach 300 tons per month (*J. Soc. Chem. Ind.*, 1901, p. 300).

A small island belonging to *New Zealand*, evidently the crater of a huge submerged volcano, which contains large deposits of sulphur, has been described by M'Ivor (*Chem. News*, 1887, lvi. p. 251). It will probably be very soon submerged as well. One thousand six hundred and ninety-two tons of sulphur were produced in that colony in 1900.

Enormous quantities of sulphur exist in the *United States of America*, but in many of the localities, where sulphur deposits have been found, these have not yet been worked at all, or the working has been given up after a period of unsuccessful efforts for overcoming the difficulty of extracting commercial sulphur from the raw ore, or on account of the distance from the places where the sulphur can be profitably utilised or sold. In 1908, as reported in *Mineral Resources of the United States* for 1909, p. 686, sulphur was commercially produced only in four States of the Union, *e.g.* in Louisiana, Nevada, Utah, and Wyoming. Sulphur has also been found in Texas. The Colorado Sulphur Company ceased working in 1908, so that this state is now excluded from the sulphur-producing states. As heretofore, the bulk of the output of sulphur came from

Louisiana (Calcasieu Parish), owing to the constant extension of the Frasch process, to be described later on. The production of Utah and Wyoming had decreased to some extent. The Utah deposits are known as the "Cove Creek beds," and are located near Black Rock Beaver County. In Wyoming sulphur is mined near Cody, and near Thermopolis. In Nevada the proprietors of the Cove Creek mine started in 1886 the working of sulphur by Dickert's process (see below), but only a few thousand tons per year are got there.

The most interesting and important deposit of sulphur is that discovered in 1902 in the Grand Gulf Basin, near Lake Charles City, in the parish of Calcasieu, State of Louisiana. Two wells have been bored at different localities, which struck sulphur at a depth of about 450 ft. The first and thickest bed of sulphur is from 108 to 112 ft. thick; in the northern portion of that deposit depths of over 500 ft. of sulphur have been reached. This layer contains near the top 62 per cent., in the centre 90 per cent. of pure sulphur. One of the wells has been continued lower down, and proved the existence of several smaller beds of rich brimstone-ore, and several hundred feet of gypsum containing sulphur; in the other well no gypsum, but calcareous substance containing sulphur is found. The working presents a difficulty, as there are several hundred feet of quicksand on the top of the brimstone-beds, which is, however, overcome by the Frasch process, to be described below. Details in the *Eng. and Min. J.*, 1904, 13th Oct., and in *Chem. Trade J.*, xxxv. p. 395.

In *Texas*, in the valley of the Brezos River, S.W. of Galveston, a large deposit of sulphur has been found, which is to be worked by Messrs S. M. Swenson & Company, who had for this purpose bought 10,000 acres of land.

The following statements on the production of sulphur in the United States (see Table, p. 27), and on the importation from abroad into the States are taken from the various volumes of the official *Mineral Resources of the United States.* The figures denote "long tons" (2240 lb. = 1016·648 kg.).

The sudden and momentous increase of the production and decrease of the importation of pyrites since the year 1904, testifies to the success of the Frasch process for the extraction of sulphur from raw ore (p. 30).

The exportation in 1909 was 37,142 tons; in 1910, 30,742 tons.

In *British Columbia*, on the Skeena River, a large deposit of sulphur has been found, and it was expected to supply the Puget Sound Country, and eventually the whole Pacific Coast, from this source (*J. Soc. Chem. Ind.*, 1901, p. 1040).

Sulphur is found also in many other places in America, *e.g.* in the volcanic regions of Ecuador and Mexico, at Chillan in Chili, and elsewhere.

Year.	Production. Tons.	Importation from Abroad, tons.			
		Crude Sulphur.	Flowers of Sulphur.	Refined Sulphur.	Total.
1891	1,071	116,971	206	10	117,187
1892	1,630	100,938	158	26	101,122
1893	1,200	107,601	241	41	107,885
1894	441	124,467	165	41	124,673
1895	1,650	125,950	581	229	128,410
1896	3,800	145,318	206	447	146,430
1897	1,690	138,846	158	148	139,313
1898	2,726	159,790	241	163	160,460
1899	1,565	140,841	165	184	141,361
1900	4,630	166,457	581	142	167,328
1901	6,867	174,194	748	262	175,104
1902	...	170,601	738	14	171,453
1903	34,396	188,990	1,854	160	191,004
1904	127,292	127,996	1,332	163	129,491
1905	181,677	82,961	572	779	84,312
1906	294,153	72,404	1,100	700	74,204
1907	293,106	20,399	1,458	606	22,463
1908	369,444	19,620	793	693	21,116
1909	239,312	28,800	770	966	..
1910	255,534	28,656	1,024	1,106	...

It has long been known that the crater of the Popocatepetl, in Mexico, contains large quantities of brimstone; and a railway has been projected in order to get at it. In the year 1884 an annual production of 50,000 tons of brimstone was expected to begin with, and vitriol-works were to be erected all along the line (*Fischer's Jahresber.*, 1884, p. 265). But a visit of two American engineers, reported in *Eng. and Min. J.*, 1904, lxxvii. p. 730, disclosed the fact that the production of new sulphur in that crater is only 120 lb. in a month!

The quantity of sulphur in Lower California (Mexico), about 50 miles from the U.S. frontier, was estimated in 1911 at several million tons, of which 60,000 tons of 45 per cent. ore are in sight. The rock is so soft that it can be won by the pick-axe and spade. At present the bed is not worked.

In *Z. angew. Chem.*, 1912, p. 366, a report is made of an enormous bed of sulphur near Cerritos, in the State San Luis Potosi, which is stated to be one of the richest in the world, and to furnish 800 tons of refined sulphur per month. The bed begins 20 ft. under the surface of the ground, and has been proved down to 190 ft., but it seems to extend "infinitely far" below. The ore contains from 37 to 90 per cent. pure sulphur; one-third of it is consumed in the country; the remainder is exported to Germany. Another, much smaller, bed exists at Venado, in the same State, it forms a layer 10 ft. thick, just below the surface, and furnishes 3 or 4 tons sulphur ore per day.

On the island of Saba, one of the Antilles, there is a bed of brimstone, yielding on an average 45 per cent. of sulphur, which was worked for some time, but had to be abandoned as not paying the expense (*Dingl. polyt. J.*, 1886, cclix. p. 43).

In Chili brimstone is found at a height of from 12,000 to 13,000 feet above the sea. The mines, which were started in September 1900, by an Iquique Company, are 54 miles from the nearest railway station. The product is said to be of very good quality; it is used in the provinces of Atacama and Tarapaca for the recovery of iodine, and for making blasting-powder for the nitrate works. This seems to be the Taltal deposit mentioned in a Consular Report, quoted *J. Soc. Chem. Ind.*, 1901, p. 1039. In 1901, the working was stopped as being at present unremunerative (*Z. angew. Chem.*, 1901, p. 1243).

In Venezuela large beds of sulphur have been found, 20 or 30 miles distant from the coast, with which they are to be connected by a wire-rope line. The beds are to be worked by the Deutsch-Venezolanische Schwefelgruben A.G., at Cologne. It is stated that the ore averages 62 per cent. sulphur.

As reported in *Chem. Trade J.*, 1912, i. p. 151, very large deposits of sulphur ore, containing about 65 per cent. of sulphur, have been discovered in South Africa, but no particulars about this are given.

The world's production of sulphur for some years is stated in the *Mineral Resources, etc.*, 1906, p. 1106, in metric tons (at 1000 kg.), as follows:—

Country.	1904.	1905.	1906.
	Tons.	Tons.	Tons.
United States . . .	129,329	184,584	298,859
Austria	2,141	1,700	4,579
Chili	3,595	3,510	4,000
France	834	740	789
Greece	1,225	1,126	1,200
Hungary	143	135	140
Italy	527,563	568,927	499,814
Japan	25,587	24,419	24,000
Spain	2,232	2,285	2,263
Sweden	35	...	...
Total . .	692,684	787,426	832,644

In this enumeration Germany and Russia are not mentioned. The former produces about 1200 tons, the latter about 500 tons of native sulphur.

No notice is taken in the above table of the production of sulphur from alkali waste and other sources by chemical processes.

A new use of sulphur, according to the *Chem. Trade J.*, 1911 (vol. xlix. p. 497), is that as a fertiliser; it acts as a disinfectant, and is absorbed in the fibre of the plants.

Manufacture of Commercial Sulphur from Native Crude Brimstone.

The old Sicilian "calcarone" method, described in all older text books, need not be described here, as it is now obsolete. On p. 18 we have quoted the books in which the former Sicilian methods are described in detail; here we shall treat only of the more recent apparatus used for the purpose of obtaining commercial sulphur from the raw ore by fusing.

In recent years the "Gill kilns" have rapidly gained ground in replacing the calcarone methods, and they increase the output of sulphur by 50 per cent. These kilns consist of an oven covered by a cupola, called a "cell"; inside there is a smaller cupola, within which a coke fire is burning. Each cell holds from 5 to 30 cub. metres of ore. There are generally six cells working in an angular battery. The gases generated in the first cell pass by lateral channels into the next; by the time the fusion is completed in the first cell, the contents of the second cell are already heated up to the igniting-point by the gases, and so on. The gases heavily charged with sulphur are not lost as in the calcarone method; the yield is much larger, the time shorter (three or four days for each cell), and as the quantity of smoke is much less, the work can be continued almost all the year round without danger to the crops. In 1888 there were only 365 cells in 40 mines, in 1894 the number had increased to 1821 cells in 225 mines; that is over two-thirds of the total.

E. F. White (*Eng. and Min. J.*, lxii. p. 536) extracts sulphur from sulphur-ores by passing the latter downwards between two conical steam-heated vessels, where the sulphur is fused and runs out at the bottom.

De la Tour de Breuil (*Comptes rend.*, xciii. p. 456) employs a 66-per-cent. solution of calcium chloride for the same purpose. C. Vincent recommends this process (*Bull. Soc. Chim.*, xl. p. 528).

K. Walter, in Milan, has patented an apparatus for continuously melting out sulphur by combustion of part of the sulphur itself, and converting the sulphur dioxide formed into sulphuric acid in lead chambers (*Chem. Zeit.*, 1886, p. 1199).

The American patents of F. Dickert, Nos. 298734 and 301222, describe an apparatus for melting sulphur, consisting of a jacketed pan connected by a perforated diaphragm with another jacketed pan turned bottom upwards. The melting is produced by means of steam introduced into the jacket.

Sanfilippo (Fr. P. 346834) utilises the SO_2 formed in the sulphur kilns by part of the S getting burned for the manufacture of sulphuric acids or otherwise.

The Frasch Process.

A complete revolution in the production of commercial sulphur from hitherto unavailable crude ores has been brought about by the ingenious process of Herman Frasch (U.S. Ps. 461429, 461430, 461431 of 1891), which is applied to the Louisiana sulphur, where quicksand makes it impossible to use the ordinary methods (*supra*, p. 26).

I heard of this process already in 1893 from Mr Frasch himself, but it took a good many years before it reached a full success

The description of its state in 1902, in the third edition of this book, pp. 18 and 19, showed that success had then been distinctly attained, and the figures, given *suprà*, p. 17, on the sudden increase of the production of sulphur in the United States, are the best demonstration of this. In February 1902 I received from the inventor (Mr Frasch) a set of photographs, taken on the spot a few weeks before, exhibiting the manufacture on a large scale, the pumps discharging a full 3-in. stream of liquid sulphur all through. The boiler-power was being increased from 2100 to 4300 H.P. Up to then the average production was 100 tons per day from one well; up to 250 tons per day had been realised before.

In 1904, as reported by the *Eng. and Min. J.*, 16th October 1904, two wells according to the Frasch system were in operation at the Sulphur Mine, Louisiana, by the Union Sulphur Co., with a daily output of 500 to 750 tons (maximum record 850 tons) of sulphur, and it was estimated that 200,000 tons would be got in that year.

Ed. Hart, in the *J. Amer. Chem. Soc.*, 1905, xxvii. pp. 158 *et seq.*, reports that 16,000 tons per month of brimstone were then taken out by the Frasch process. As much as 23,000 tons have been taken out of one well. The existence of 40,000,000 tons has been proved. The holes are drilled to a depth of 800 ft., and a 13-in. casing is driven in. Inside this a 10-in., then a 3-in., and finally a 1-in. pipe are inserted. Between the 3- and 10-, and the 10- and 13-in. pipes superheated water is forced into the well by its own expansive force. The sulphur melts and rises to 400 ft. in the 3-in. pipe, from which it is raised to the surface by compressed air through the 1-in. pipe. The molten sulphur is run upon the ground in ponds made of rough boards, 72 ft. square and 14 ft. high. It costs $2·90 f.o.b. per ton.

In November 1904 it was reported that the mines were shipping about 800 tons daily, the maximum being 860 tons.

New patents taken out by H. Frasch in 1905 (U.S. Ps. 799642 and 800127) describe the process as follows. Water is heated to a temperature above that at which molten sulphur begins to darken, by bringing it in contact with high-pressure steam, and is then, together with the water of condensation, forced by steam-pressure through two concentric pipes into the deposit. The outer pipe opens near the upper part of the mine cavity, whilst the inner one is closed at the bottom, but has a discharge outlet, a little above its closed end, opening near the lower part of the mine cavity. The hot water melts the sulphur and passes away through the porous rock, means being provided to prevent its return to the surface of the ground. The molten sulphur separates by gravity from the water, and is forced, by the steam-pressure, up through an inner pipe, which passes down through the closed end of the smaller hot-water pipe, and is provided at its lower end with a strainer. The hot water entering the mine cavity is kept under a steam-pressure less than that of a column of molten sulphur, equal to the depth of the deposit below the level of the ground; compressed air or the like is forced through a pipe, provided at its discharge end with a perforated piece of a metal not corroded by molten sulphur, whereby the density of the latter is reduced to near or below that of water, and the molten sulphur is then readily forced up to the surface of the ground by the available pressure in the mine cavity.

Frasch's Amer. Ps. 870620 and 988995, contain some further improvements in details of his process. Into the underground sulphur deposit steam is injected at a temperature at which the melted sulphur begins to be pasty when further heated; the sulphur is then raised in the molten condition. According to his Amer. P. 1008319, of 14th Nov. 1911, a well is sunk into the underground sulphur deposit, and a retaining wall is formed above the well-hole by introducing sand or other suitable perforated lining; the sulphur is then liquefied within the retaining wall (for instance, by introducing hot water, which is allowed to flow away underground), and is removed in the liquid state.

In 1905 I received direct information (as I reported in *Z. angew. Chem.*, 1905, pp. 1009 and 1106) on the state of the Frasch process from the Union Sulphur Company in New York which works that process. That firm then owned forty-eight steam-boilers of 150 H.P. each, = 7200 H.P., for raising the necessary steam and heating the water to the temperature required, as described by Hart, *supra*. The boilers are fired with Beaumont oil (naphtha).[1] Although this method of firing requires very little manual labour, there were 600 men employed at four or five wells going day and night. The average production exceeded

1000 tons per day. A sample of that sulphur, transmitted to me, showed 99·6 per cent. real S. The production at those Louisiana works, say 350,000 tons per annum, already reached two-thirds of the Sicilian production. According to further information, given by Mr Frasch personally to me in April 1905, they had then at the mines steam-boilers for 13,500 H.P., and a tank of 200,000 barrels' capacity for the heating-oil. Four sets of sulphur wells were then in operation; and a fifth was to get to work within two months. Each set of wells easily produces 400 tons of sulphur in twenty-four hours, but may be worked up to 630 tons, so that a daily production of more than 3000 tons would be possible.

In 1909, according to *J. Ind. and Engin. Chem.*, 1911, iii. p. 355, the output of sulphur in the United States had risen to 339,312 long tons (from 3147 tons in 1900), and of this 37,142 tons was exported, against a large importation in former years. This enormous reversal of conditions, it is stated, is due to the Frasch process.

A set of photographs of sulphur mines in Louisiana, which I have now (1911) before me, illustrate the progress of the process very strikingly. It shows blocks of sulphur, 500 ft. long, 250 ft. wide, and 65 ft. high, obtained by running the sulphur, driven up from the mine through the Frasch pipes, into this enormous reservoir. When this block is completed to 65 ft. high, it is permitted to congeal; the boards forming the sides are taken off, and the sulphur is made available for shipment by blasting. Locomotive cranes pick up 2½ tons of sulphur :o load the cars; the time necessary for this purpose has been 'ecently much reduced. The harbour from which the sulphur ;hips leave the gulf is Sabine. A mechanical loading-device oads the ships at the rate of 1000 tons per hour, so that a ship)f 8000 tons, arriving in the morning, can go to sea with a full argo before nightfall.

In December 1911, Mr Herman Frasch received for his mmense technical achievements the great distinction of the 'erkin medal. The speech of Professor C. F. Chandler and the eply of Mr Frasch, which are recorded in *Journ. Indust. and 'ngin. Chem.*, 1912, pp. 131 to 147, give a most interesting ccount of his inventions and their practical application.

The Union Sulphur Company has entered the business of refining sulphur in France; it possesses two refineries, in Marseilles and Cette, the French vineyards using enormous quantities of refined and ground sulphur. These refineries now produce about one-third of the total amount of sulphur consumed in France.

Other Recent Processes for the Extraction of Sulphur from Raw Ores.

Lalbin (Fr. P. 333094) extracts sulphur from earths and especially from tar or woody matters, by means of a vertical retort, heated from a furnace by means of surrounding flues. A certain quantity of air is blown into the retort, in order to oxidise gases which might otherwise form explosive mixtures [?]

Roos (Fr. P. 354688) heats earth or sand containing sulphur above its melting-point and separates it from the earth, etc., by centrifugal action.

E. F. White (Amer. P., 847869) describes an apparatus for sulphur smelting, Fig. 1, which consists of a cylinder, 2, with

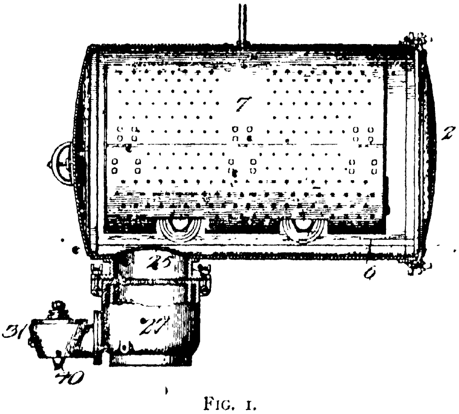

Fig. 1.

tracks, 6, secured in its lower portion. On these travels an ore-charging car, 7, constructed of perforated metallic sections, a number of which can be independently moved and are provided with dumping-sections. A sump, 25 to 27, communicating with the cylinder, is provided with means for heating and a tap-valve, 31, with a plug, 40.

Fleming (Amer. P. 945926) melts the ore by any means whatever, and afterwards maintains it in fusion by electrical means, out of communication with the atmosphere, forcing currents of steam, with or without air, through the molten mass, and condensing the vapours evolved in cooled receivers.

Sanfillippo di Luigi (Austr. P. applic. A4913 of 1910) describes an apparatus for the distillation of sulphur from its ores, consisting of an inclined still, fitted with baffling plates which compel the ore to keep along the bottom side of the still, and heated all over its circumference in order to prevent any condensation of sulphur vapours at the still sides.

Rocasolano (*Rev. real acad. scien.* Madrid, viii. 895; extract in *Abstr. Amer. Chem. Abstr.*, 1911, p. 3501) first attempted to modify the process of Thomas, who melts out the sulphur by superheated steam, by substituting for the steam, air heated above the melting-point of sulphur by means of a tubular system through which circulates steam at a pressure of seven atmospheres. This modification was open to most of the objections to the Thomas process, and, moreover, cannot be recommended on account of the small heat capacity of air. The following process was then devised and is now in use industrially in several parts of Spain. This method secures extraction of sulphur and refining part of it by a single fusion. A cylindrical boiler, holding about 640 kg. of mineral, and having an opening near the top for loading, is inclined at an angle of 40 to 45°. The mineral is held in place by a movable grating near the lower end, and below this grating the cylinder is terminated by an elbow dipping under water. Where heat is applied, a portion of the sulphur melts, and carrying with it organic bituminous material volatile at 120° to 130°, flows out of the elbow of the cylinder and is collected under water as fused black sulphur of 97 to 98 per cent. purity. As the temperature rises, sulphur is volatilised and carried through the upper end of the heater into a cool chamber, where it is obtained as flowers of sulphur, as well as through the lower end of the cylinder, where it is collected in yellow masses of 92·2 to 99·7 per cent. purity. Air is excluded from the apparatus by means of water-seals at all openings. All the principal commercial forms of sulphur may thus be obtained in one operation, and the proportion of each form may be varied at will within certain limits. The following is a typical single operation: from 600 kg. of mineral containing 30 per cent. sulphur were obtained 12 kg. flowers of sulphur and 155 kg. of fused sulphur of the second and third commercial grades, making a total yield of 92·7 per cent.

Sulphur Manufactured from Various Materials.

Free sulphur is produced in large quantities in the manufacture of *coal-gas*, and is contained in the *spent oxide of iron.* We shall treat of this later on as material for producing sulphur dioxide; in this place we mention it only as a source of obtaining free sulphur. This is sometimes done by extracting it with carbon disulphide; but this process does not generally seem to pay (cf. *J. Soc. Chem. Ind.*, 1883, p. 491).

Gerlach (Ger. P. 229 of 1877) proposed to obtain sulphur from sulphur-ores, and especially from the spent oxides of gas-works, by heating them in iron or fire-clay retorts, whilst at the same time superheated steam is passed through. The sulphur is said to distil very rapidly. A description of this process, with diagrams, is found in Wagner's *Jahresber.*, 1879, p. 268. It was tried in Upper Silesia, with sulphur marl, but did not answer (*Fischer's Jahresber.*, 1882, p. 234).

O. C. D. Ross patented a process in every way similar to Gerlach's (E. P. 713 of 1879). Other processes of the same kind are described in the *Scientific American*, xxxix. p. 276, and in the *Chem. Zeit.*, 1879, p. 241, by Dubois (B. P. 13108 of 1885 and 7129 of 1886; Ger. P. 41718: the last patent describes a revolving retort).

Broadberry (*Gas World*, 1895, xxiii. p. 643) extracts the sulphur from spent oxide of gas-works by means of benzol at a temperature of 70° or 80° C., employing a circulating-apparatus. One gallon of hot benzol yields on cooling 2·5 to 2·75 lb. of solid sulphur, and retains 0·25 lb. in solution, which is obtained in distillation. From an experiment with 20 lb., he calculates a profit of £1, 6s. 3d. per ton of spent oxide.

The sulphur made from gas oxide is mostly of a dark colour, owing to the presence of a very small quantity of tarry substances, and this makes it very difficult to sell, so that it is nearly always burned without extracting it, as we shall see *infrà*, No. 5.

In order to remove this dark colour, Bécigneul (Ger. P. 178020) filters the benzolic or toluolic solution through animal charcoal. He describes an extracting apparatus in the form of an autoclave, a charcoal filter, a cooler, and a filter for collecting the sulphur, of such a construction that the benzol may be recovered. The desulphurised mass is treated with lime in a high-pressure apparatus, in order to recover the cyanogen compounds. His B. P. 8530 of 1905 prescribes extracting the sulphur by hot toluol, allowing it to separate by cooling, and using the solvent over and over again. In his Austr. P. 27298 he prescribes mixing the toluol with carbon tetrachloride.

Cornillaux (B. P. 7616 of 1905) purifies the solution of sulphur in CS_2, obtained from spent gas oxides, by filtration through coke, soaked with concentrated sulphuric acid.

Maybluh (Ger. P. 148124) extracts spent gas oxide with petroleum, boiling over 150°, say at 250° at boiling heat. The fusion of the sulphur greatly assists its solution, so that the petroleum can take up 110 per cent. sulphur, and this is obtained of yellow colour, free from tar, and can be easily further purified by distillation.

Vaton and Zuaznavar (Fr. P. 336661) distil the material in retorts, with a condensing chamber of such dimensions that the temperature is maintained between 150° and 440°, so that only pure sulphur is condensed therein.

Gunther and Franke (B. P. 11187 of 1907; Fr. P. 377827) extract sulphur from gangue or other material, especially spent oxide of gas-works, by boiling acetylene tetrachloride, as a mixture of it with xylol; on cooling all the sulphur separates except 1 per cent. remaining in solution. The ferric oxide remaining behind may be used over and over again, and thus accumulates a greater amount of cyanogen compounds than is possible with other sulphur-extracting methods.

Derome (Fr. P. 372099) heats the material to redness, with or without the addition of a hydrated base, with injection of steam into the retort, to assist in decomposing cyanides. Sulphur, ammonia, etc., escape and are condensed in a cooling-chamber by water sprays.

P. E. Williams (B. P. 596 of 1909) treats the spent oxide with liquor ammonia, and filters the solution of ammonium polysulphide from the ferrous sulphide, which is converted into oxide by exposure to the air and again treated with NH_3. Sulphur is precipitated from the ammonium polysulphide solution by boiling, the escaping NH_3 being recovered in any suitable manner.

Gouthière and Duvancel (Fr. P. 427892) extract the sulphur from spent oxide by a solution of sulphide NH_4, K, Na, Ba, or Ca, and decompose the polysulphide solution formed by heat or by CO_2 and lime, so as to separate the sulphur and to recover the purifying material. According to Their (Fr. P. 434673) they recover at the same time ammonia from the cyanides present.

It is not possible to obtain sulphur entirely free from the solvent, *e.g.* that obtained from spent gas oxides, as petroleum, aniline, tar oils, and especially carbon disulphide, by mere distillation. The Chemische Fabrik Phœnix, Rohleder & Co. (Ger. P. 182820, and B. P. 23957 of 1906; Fr. P. 370893) attains this object by running the solution, in a finely divided form, into water heated above the boiling-point of solvent; in the case of CS_2 say to 70°, at such a rate that no large quantity of the solvent can collect there. The small quantities gradually flowing in quickly give up the CS_2 by evaporation, and the S collecting at the bottom of the vessel in the form of leaflet does not retain any CS_2. When enough S has collected, the supply of solution is stopped and the boiler is heated to about 85° for ¼ hour, then allowed to cool and emptied; the sulphur remains on a sieve placed below.

A certain quantity of sulphur is obtained by the *distillation of pyrites*. This, however, pays in very few places, except under special circumstances—for instance, at the works of J. D. Starck in Bohemia, which formerly supplied nearly all the fuming oil of vitriol, and where the distillation of pyrites is practised in order to obtain a material for the manufacture of sulphate of iron. Between 1863 and 1872, 2440 tons of sulphur were thus made. The distillation takes place in earthenware tubes 3 ft. 3 in. long, 5 in. high, and 5½ in. wide, quite open at the back, and in front narrowed to an opening of ¾ in. diameter; they are glazed with common salt; and three tiers of seven tubes each are placed in each furnace. For each tube there is a small receiver of sheet-iron half filled with water, and attached to the tapering end of the tube. The charge of pyrites is put into the open end; a slanting piece of sheet-iron is placed in front; and the opening is closed with sand or pyrites cinders, as shown in Fig. 2.

Here only one-third of the sulphur contained in the pyrites is recovered; but in Sweden half (?) of the sulphur is said to be obtained in a furnace built similar to a lime-kiln, and continued at the top in a wooden chimney serving as a condensing-space. The kiln, having been first made red-hot, is charged with pyrites, of which one portion is burned whilst the other portion volatilises and is condensed at the top. The work is carried on continuously, fresh pyrites being from time to time introduced through an opening near the top, and the cinders being removed at the bottom.

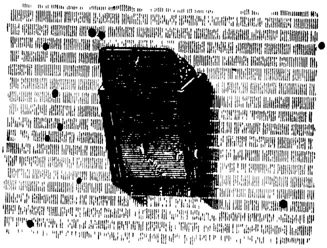

FIG. 2.

P. W. Hofmann (*Dingl. polyt. J.*, ccxx. p. 232) proposed to utilise the sulphur of the pyrites smalls. If sulphur dioxide is conducted over red-hot calcium sulphide (from alkali-waste), it is at first completely absorbed; afterwards sulphur distils over, and the calcium sulphide is transformed into sulphate. The latter, by conducting ordinary coal-gas over it in a red-hot state, or by mixing it with coal and igniting, is reconverted into sulphide, which can be used over again. Hofmann proposed to burn the pyrites smalls at the mines, to obtain their sulphur by means of calcium sulphide in a state fit for sale, to treat the cinders by a process to be described in a later chapter for zinc chloride and sodium sulphate, and to work the residue for pig-iron in a blast-furnace. This proposal has not found any application in practice, and is not likely to do so, since the burning of pyrites dust by the shelf-furnace is quite as advantageous for acid-making as that of lump ore.

According to a French patent of the Société de St Gobain (No. 107820 of 28th April 1875), on the top shelf of an ordinary shelf-burner for pyrites smalls (see Chapter IV.) a fire-clay retort is to be placed, in which the pyrites is first deprived, by distillation, of a portion of its sulphur, which is collected in the well-known condensing-chambers as flowers of sulphur. After some time the partially desulphurised pyrites is let down to the next lower shelf, and so on to others lower down. Here the remainder of the sulphur burns, and the gas goes into acid-chambers, whilst its heat causes the distillation of further portions of pyrites in the retort. This process does not answer: the flowers of sulphur obtained are very acid; and both the burner and the chambers work very badly. A similar process has been again patented by Labois (E. P. 9761 of 1884).

Buisine (Ger. P. 73222) heats half-roasted pyrites with sulphuric acid, to recover sulphur, ferrous sulphate being obtained as by-product. According to P. 79706, the pyrites is to be distilled in closed vessels at 700° C. and the residue treated as above with sulphuric acid. The residue, consisting of sulphur and ferrous and cupric sulphate, can be applied as it is to vines for certain diseases; or else it is extracted with water, the residue is worked for sulphur, and the solution, by treating it with metallic iron, yields metallic copper and ferrous sulphate.

Holloway's process (B. P. 500 and 1131 of 1878) at one time excited much attention. He blows heated air through melted iron sulphide, thus decomposing it into a cupreous matt and a slag, together with free sulphur, which distils off and can be collected. The principal aim of this process was the concentration of poor copper-ores in countries where fuel is expensive. It has been described by the inventor in a paper read before the Society of Arts, which has been published together with the discussion following the reading of the paper. Bode (*Dingl. polyt. J.*, ccxxxii. p. 433) has criticised it. Dr Angus Smith (*Alkali Reports*, 1877-78, p. 47) expected important results from this process, which is decidedly very interesting; but it has found no practical application.

Stickney (*Eng. and Min. J.*, lxv. p. 674) heats pyrites to red heat by means of producer-gas. There is an escape of H_2S and SO_2, which are converted into free sulphur by means of a spray of salt solution (*cf.* Schaffner's and Helbig's process, Vol. II. 3rd edition of this work, pp. 935 *et seq.*); the reaction is to be promoted by electric sparks.

Swinburne (Ger. P. 134734) places the sulphide ore in a bath, consisting of fusible chlorides of heavy metals, heats to a high temperature and applies the electric current which produces free chlorine from the chlorides. The chlorine decomposes the sulphide with liberation of sulphur which distils off, metallic chloride being reformed.

Malzac (Ger. P. 163453) obtains sulphur from the sulphide ores of copper, zinc, and other metals by digesting them with an ammoniacal solution in the presence of air.

Fröhling, Fleming, and Whitlock (B. P. 19295 of 1900) profess to obtain practically all the sulphur from FeS_2 by heating the ore in a retort in a stream of carbon dioxide or nitrogen with the addition of a small regulated quantity of oxygen, by which only the iron is burnt to Fe_2O_3, the sulphur being set free.

Walter (Ger. P. 192518) obtains sulphur in the roasting of pyrites smalls, by a furnace similar to the Herreshoff burner (Chap. IV.) but fitted in a special way, so that the condensing sulphur remains in a melted state and can be run off through one or more lateral pipes. Or else the roasting takes place in slightly inclined revolving cylinders. His process for obtaining both rolls and flowers of sulphur directly from the ores will be mentioned later on.

Roos (Fr. P. 354688) obtains sulphur by centrifuging minerals containing it at a high temperature.

Lalbin (Fr. P. 353830) sublimes sulphur from minerals by means of a furnace heated by producer-gas.

Fleischer (Ger. P. 205017), while distilling off a portion of the sulphur in pyrites, leads air and steam into the roasting furnace, whereby the residual sulphide is decomposed with formation of H_2S and SO_2. The gases from the furnace, containing excess of steam, are cooled first to a temperature above 100°, in order to condense the sulphur vapour, and are then further cooled, and if necessary water is added in order to cause the reaction:

$$2H_2S + SO_2 = 2H_2O + 3S.$$

The Consortium für elektrochemische Industrie (Ger. P. 162913) obtains sulphur from the sulphides of the alkaline earth metals (Ba, Sr, Ca) by treating them with chlorine, whereby the chlorides of these metals are formed.

It has often been proposed to prepare sulphur by *passing gases containing sulphur dioxide through red-hot coal (coke).* A special apparatus for this purpose has been proposed by Haenisch and Schroeder (B. P. 6404 of 1885). They pass the gases through fire-clay cylinders filled with coke and heated from the outside by producer-gas; the products of combustion travel through another cylinder, filled with open brick-work and heated by the waste fire-gases of the first operation; here the undecomposed SO_2, the carbon monoxide, carbon disulphide, and carbon oxysulphide act upon one another, so that, if the current has been properly regulated, ultimately only CO_2 and S are formed. Or else the SO_2 is at once treated with CO, according to the equation

$$SO_2 + 2CO = 2CO_2 + S.$$

This process has been tried on a large scale at Oberhausen (cf. *Chem. Zeit.*, 1886, p. 1039, abstracted in *J. Soc. Chem. Ind.*, 1886, p. 534), but evidently not successfully.

J. and F. Weeren obtain the SO_2 for this purpose by calcining sulphates with silica (Ger. P. 38041). They describe a special apparatus for this reduction and the reduction of the SO_2 by incandescent coke to S.

Heinrici (*Z. angew. Chem.*, 1898, p. 525) employs this reaction for the purpose of utilising the acid tar formed in the purification of mineral oils. By heating this SO_2 is evolved, which is reduced to free S by red-hot coke.

Baggaley (Amer. P. 805701) obtains the sulphur contained in certain smoke gases by filtering them through a travelling combustible filter and burning the whole in order to obtain sublimed sulphur.

The Soc. an. Metallurgique "Procédés Laval" (Ger. P. 196604) reduces SO_2 from gases containing it to free sulphur by carbon monoxide. The SO_2 gases are introduced into the furnace centrally, and the CO, or a corresponding mixture of fuel and air, tangentially, which causes a complete mixture, forming CO_2 and free S, the latter being afterwards condensed by suitable means.

F. R. Carpenter (Amer. Ps. 871912 and 925751) obtains sulphur from the roasting-gases of sulphide ores (especially in the Colorado district). The gases are purified from flue-dust in chambers, where they are also saturated with water introduced as spray; they are then cooled in large chambers by means of water-coils, which causes all the SO_2 to condense as an aqueous solution; the residual gases are taken away by an exhauster. The solution of SO_2 is freed from flue-dust, and the SO_2 boiled out of it by means of coils containing water superheated in the flue-dust chambers. The SO_2 is conducted into towers, containing red-hot coke, where both SO_2 and H_2O are reduced as follows, with formation of CO_2 or CO:

$$2SO_2 + 2H_2O + 3C = 2H_2S + 3CO_2$$
$$SO_2 + H_2O + 3C = H_2S + 3CO.$$

This gaseous mixture, after admitting the necessary amount of air, is worked in Claus-kilns (*vide* our Vol. II. 3rd edition, pp. 972 *et seq.*) for sulphur:

$$H_2S + O = S + H_2O.$$

A modification of the process, which is, however, less advantageous, consists in taking the roasting-gases, without concentrating the SO_2 in the above described manner, with addition of steam directly into the reducing-kilns, or else they are further heated to decompose the "subsidiary sulphides."

P. S. Smith, assignor to the Pont de Nemours Powder Co. (Amer. P. 878569), forms producer-gas and water-gas successively, and mixes the water-gas with the SO_2 contained in sulphur-bearing gases. This mixture is highly heated by the producer-gas; the sulphur vapour, set free by the reaction between the SO_2 and the water-gas, is condensed and collected. The same inventor (Amer. Ps. 945111 and 945112) describes special constructions of apparatus for this purpose, which allow of working the process in a continuous manner.

Sulphuretted hydrogen has been very frequently proposed as a material for the production of free sulphur, which has become an economical possibility through the Claus process for the recovery of sulphur from Leblanc tank-waste. We cannot describe this industry in this place; it is fully dealt with in Vol. II. part ii. of the 3rd edition of this work, pp. 967 *et seq.* (1909), and we subjoin only a brief notice of some recent processes.

Carulla (*J. Soc. Chem. Ind.*, 1897, p. 980) prefers burning H_2S in an ordinary pyrites-kiln, in lieu of the Claus-kiln, as the yield is much larger.

Baranoff and others describe (E. P. 7269 of 1898) the production of S from H_2S, obtained by the reduction of native sulphates and treatment by CO_2. This H_2S is passed over red-hot sulphates, which are thereby reduced and yield free S and SO_2.

The Chemische Fabrik Rhenania and P. Projahn (Ger. P. 173239) pass the gases containing H_2S, *e.g.* those from the

Claus process, after mixing them with oxygen or air, through a cupola charged with bauxite or other material containing aluminium oxide, which need not be previously heated, as it gets up by itself to the necessary heat; there is no danger of explosion in this case, such as have taken place when employing iron oxides as a contract substance for a similar purpose, and much less H_2S is lost in heating-up. The reaction here occurring is:

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

The Chemische Fabrik Rhenania (*Chem. Zeit.*, 1908, p. 247) states that in the recovery of sulphur from Claus gases the application of bauxite as contact mass in this manner on the large scale allowed to recover the sulphur up to 5 per cent., whilst an experiment on the larger scale with titanic iron ore (B., P. 25976 of 1906), to be mentioned just now, did not confirm the good results obtained in the preliminary experiments.

Tyers, Hedley, and the United Alkali Co. (B. P. 25976 of 1906) use a salt or ore of titanium as the catalytic agent in the recovery of sulphur from H_2S.

Hellsing (Fr. P. 376534; Ger. P. 209960; B. P. 8164 of 1907) brings the gases containing H_2S into contact with a strong solution of SO_2; after the precipitated sulphur has been deposited, the liquor is again treated with SO_2. In order to prevent formation of a colloidal solution of the sulphur set free, sulphuric or hydrochloric acid, or a suitable salt, are added to the solution of SO_2.

Burschell (B. P. 11133 of 1906) decomposes gases containing H_2S by an alkaline solution of ferric salts as FeS, and recovers from this S and $Fe(OH)_3$, which is dissolved in alkaline solutions, containing sugar or tartaric acid, and used over again for precipitating FeS.

Very similar to this is the Ger. P. 181063 of the Gewerkschaft Messel.

The 47th *Inspectors' Report on Alkali Works* (for 1910), pp. 23-26, contains a paper by Mr Linder on the oxidation of H_2S by MnO_2 in absence of CO_2 and presence of air, the result of which is that the presence of free lime ($Ca(OH)_2$) is favourable to a high yield of free sulphur; the yield of thiosulphate in this case is low, and there is an entire absence of MnS and polysulphide.

Lang and Carson (*Proc. Chem. Soc.*, 1905, p. 160) made a laboratory study on the reaction between H_2S and SO_2, which did not produce any fresh results.

Burkheiser (Ger. P. 220632) converts about a third of the H_2S into SO_2 by passing the gases over an oxygen carrier, and then brings about the well-known reaction:

$$2H_2S + SO_2 = 3S + 2H_2O.$$

From the *sulphides of alkaline earth metals* (Ba, Sr, Ca) the Nurnberg Consortium für elektroch. Industrie (Ger. P. 162913) obtains sulphur by treating them with chlorine at higher temperatures, until the chlorine contained in the distillate in the form of sulphuryl chloride suffices for chlorinating the polysulphide formed, whereupon this is decomposed by the sulphuryl chloride in aqueous solutions to chlorides and free sulphur.

Palaschkowski (Russ. P. 5464 and 5477 of 1901; *Chem. Zeit.*, 1902, p. 15) describes the following modifications of the process of Baranoff and Hildt for obtaining S and SO_2 from *sulphates.* Instead of simply mixing the sulphates with coke, he moulds them into briquettes by means of coal-tar, etc., which shortens the time of reduction. The sulphide is decomposed by CO_2 at a pressure of 2 or 3 atmospheres. The H_2S is best not passed at once through red-hot sulphates, but first through a solution of the sulphides, which forms $Ca(SH)_2$ and NaHS. The former is converted by means of Na_2SO_4 into NaHS, which with CO_2 gives H_2S and $NaHCO_3$. Only this H_2S is employed for being oxidised by sulphates to S and SO_2.

Müntz and Nottin (Fr. P. 375469) patent the universally known process of reducing calcium sulphate in some way to sulphide, decomposing this by the CO_2 formed, and obtaining S from the H_2S given off.

Feld (B. P. 3061 of 1909; Amer. P. 985667) produces sulphur from H_2S and SO_2, by treating them with compounds of a metal (Zn, Mn or Fe), the sulphide of which is insoluble and is decomposed by SO_2, either alone or in the presence of air or oxidising agents, with formation of free S. The process is specially adapted for the purification of coal-gas, and apparatus is described for that purpose. The same inventor's

Ger. P. 192533 describes several processes for washing H_2S out of gases, with recovery of the washing-agent. His Ger. P. 237607 prescribes bringing H_2S and SO_2, mixed with each other or one after the other, into contact with moist or dissolved sulphides, thiosulphates, or polythionates of zinc, manganese, or iron.

The same inventor (B. P. 2719 of 1908; Amer. P. 927342 of Feld and Jahl; Ger. P. 202349; Fr. P. 387438) performs the interaction of H_2S and SO_2 in the presence of a substance capable of dissolving the liberated sulphur, preferably heavy coal-tar oils heated up to 40°. The temperature rises above this by the reaction. When the amount of free sulphur reaches 50 to 60 per cent., the bath is allowed to cool, the crystallised sulphur is separated centrifugally, washed with steam and the precipitated sodium sulphate dissolved out by the condensation water. Pure sulphur is thus obtained. The liquid is kept acid, in order to avoid the formation of thiosulphates and polythionic acids.

Reducing Sulphur to Fine Powder by Grinding.

Apart from sublimed sulphur (see below) very much sulphur is reduced to a fine powder by mere grinding and sifting, which operation, if performed in the ordinary way, need not be described here. We shall merely mention some special processes for this purpose.

A. Walter (Ger. P. 136547) performs the grinding and sifting of sulphur in an atmosphere of inert gas which is made to circulate through the apparatus. In this way the formation of sparks is avoided, and the sulphur can be reduced to such a degree of fineness that it passes through a sieve of 5000 meshes per square centimetre.

Köhler (Ger. P. 192815; Amer. P. 898378) obtains sulphur in a state of great fineness by dissolving it in its own weight of fused naphthalene, and after cooling removing the naphthalene by gentle heating or by extraction with a solvent.

Ducancel and Gouthière et Cie (Fr. P. 401967) incorporate finely divided sulphur with barium, strontium, or calcium saccharate, and thereby render it miscible with water, for the treatment of the vine-disease.

Marcille (*Comptes rendus*, 20th March 1911; *Chem. Zeit. Rep.*, 1911, p. 426) ascribes the action of sulphur on the oidium to the sulphuric acid contained in various quantities in finely divided sulphur. Hence the action of "extra sublimed" sulphur is strongest, whereas ordinary sublimed or ground sulphur contains only 0·01 to 0·02 per cent. H_2SO_4 and is less active. He therefore recommends passing sulphur dioxide into the condensing-chambers, in order to prepare a quality specially adapted for destroying the vine-disease.

Estimation of the Degree of Fineness of Ground Sulphur.

Since for the purpose of preventing the grape-disease (the *Oïdium*) the degree of fineness of ground sulphur is very important, in France this is ascertained by Chancel's *sulphurimeter*, shown in Fig. 3 on a scale of 1 : 2. This is a glass tube sealed at the bottom and closed at the top by a ground-in glass stopper. It is 23 cm. long and 15 mm. wide, and divided into 100° of ¼ c.c. each, beginning from the bottom; the 100° occupy a space of 100 mm.

If ground sulphur is shaken up with anhydrous ether it forms, after settling down, a layer, the height of which corresponds to the fineness of the powder. The sulphur to be tested is passed through a sieve with meshes 1 mm. wide; 5 g. of it are put in the tube, together with ether of 17°·5 C., or very nearly that temperature, filling half the tube. The tube is well shaken to break up all small lumps, more ether is poured in up to 1 cm. above the degree 100, the tube is again shaken and placed in a vertical position. When the layer of sulphur ceases to subside, its height is read off and stated as "degrees Chancel."

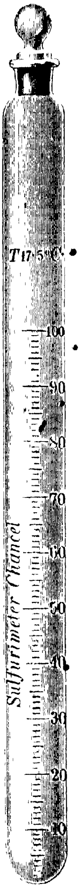

FIG. 3.

Ordinary ground and sifted sulphur shows 50° to 55° Chancel, finer grades 70° to 75°. The finest grade is obtained not by sifting, but by "fanning." This "zolfo ventilato" shows 90° to 91° Chancel (Walter, *Chem. Zeit.*, 1901, 539). For use in vineyards the "flowers" ought to show at least 60° Chancel; some demand as much as 75° Chancel.

H. Fresenius and P. Beck (*Z. anal. Chem.*, xlii. p. 21) draw attention to some points necessary to observe. The Chancel test for the degree of fineness should be made with ether distilled over sodium. After shaking up all agitation should be avoided; the sulphurimeter should be fixed in a stand and at once immersed in water of 17°·5 C. Organic matter and ashes should be estimated at little over 200° C. after evaporating the sulphur. The microscope will show whether a mixture of ground sulphur and flowers of sulphur is present. The temperature in estimating the water by drying should not be above 70° C. The authors found in several samples of Sicilian sulphur from 0·02 to 0·26 per cent. ashes, 0·02 to 0·05 per cent. organic substance, 0·17 to 0·64 per cent. residue insoluble in CS_2, of which 0·13 to 0·28 was sulphur, and 0·16 to 0·405 per cent. insoluble in caustic soda solution sp. gr. 1·2.

Refining of Sulphur: Roll and Block Sulphur.

We here mention a few modern improvements of these well-known operations.

Albright and Hood (B. P. 11988 of 1894) purify sulphur by heating it for some time just below its boiling-point.

Boude et fils (Fr. P. 408512) describe the manufacture of sulphur cast into moulds, by distilling the crude sulphur from a cast-iron retort into a cast-iron condenser, surrounded by a fire-space, and connected with a second condenser. The condensed sulphur flows from the first into the second condenser, and from this into the moulds.

Flowers of Sulphur.

We shall not describe the well-known operation of obtaining flowers of sulphur by the process of sublimation in its old form, but we must mention recent improvements in this line.

Davidson and the United Alkali Company (B. P. 17476 of 1897, and 7088 of 1898) describe some modifications of the process of subliming sulphur.

Walter (Ger. P. 177281; Amer. P. 873812) manufactures flowers of sulphur, not in the ordinary way of aspirating the vapours from the retort by an inert gas and allowing them to condense in cooling chambers (which yields various degrees of fineness, according to the distance from the retort; but by driving on the gases by means of a face-blast through the coolers so that the gases and vapours are thoroughly mixed, and the sulphur vapour is ultimately condensed in the state of uniform fineness, without drops and stalactites, of which, by the old process, sometimes 30 or 40 per cent. of the sulphur are found near the retorts. This product is sold as "zolfo ventilato."

The same inventor (Ger. P. 192472) obtains both melted sulphur and flowers of sulphur directly from the ore by passing it continuously through a vertical cylinder, together with hot inert gases (*i.e.* smoke gases), and drawing off the vapours. The inert gases may have a temperature of only 150° in the upper part, but about 350° in the lower part of the cylinder.

The Soc. an. métallurgique "Procédés de Laval" (Ger. P. 168870), in the distillation of sulphur, condense it in a horizontal cylinder provided with an agitating shaft, and surrounded by another cylinder containing a hot calcium chloride solution, so that the temperature in the inner cylinder is 115° to 125° and the sulphur remains in the liquid state; it is reduced to a state of great fineness by the agitating blades dipping into it.

Boude et fils (Fr. P. 361874), in the production of flowers of sulphur, arrange for each subliming furnace two cooling chambers, so that each of them can be emptied without interrupting the work.

The same firm (Fr. P. 369089) provide the sublimation chambers with arches, ranged perpendicularly to the breadth of the chamber, rising to the right and left of the inlet opening for the sulphur vapour.

Basse-Courbet (Fr. P. 366280), in working sulphur minerals containing arsenic for flowers of sulphur, continually draws the non-condensing gas away from the chamber by means of a fan.

Dementieff (Fr. P. 351981) introduces sulphur vapours, together with steam or sprayed water, under pressure, into a chamber where the sulphur is at once condensed in a very fine state of division.

Consoli (B. P. 8757 of 1902; Fr. P. 316226) sublimes sulphur by a continuous process in a battery of several retorts, fed with melted sulphur.

Bert (Fr. P. 401023) effects the continuous sublimation of sulphur by means of an apparatus comprising a hopper, from which the crude material is automatically fed into a vessel, heated by waste heat, in which it is melted, the impurities being deposited and removed, the liquid sulphur rising through a filtering device immersed in the liquid. The nearly pure sulphur then passes to tubular retorts of thin steel or iron, the surface of which may be suitably protected, from which the sulphur vapour passes to the collecting chambers through condensers cooled by water.

Ducancel and the Société H. Gouthière et Cie (Fr. P. 401067) make flowers of sulphur directly miscible with water by the addition of saccharates of barium, strontium, or calcium.

The process of Rocasolano, by which in one operation both brands of ordinary brimstone and also sublimed sulphur is obtained from the ore, has been mentioned, *suprà*, p. 35.

Sulphur in Special Forms (Colloidal, etc.).

Sulphur or selenium in a colloidal form is obtained by Chemische Fabrik von Heyden (Ger. P. 167664) by precipitating the sulphur from its solutions in the well-known way in the presence of albuminoid substances, redissolving in a weak solution of alkali and precipitation by alcohol, alcohol-ether, or acetone. Their Ger. P. 201371 prescribes dissolving the sulphur in physical solvents, and precipitating it again by dilution with weak solutions of albumen, or removing the solvent by dialysis or decomposition. The sulphur thus obtained is soluble in water and is valuable for medicinal purposes, *e.g.* against skin diseases. Himmelbauer (*Chem. Cbl.*, 1909, ii. 790) prepares colloidal sulphur by the action of gelatine or of colloid silica on a solution of sulphuretted hydrogen. Sarason (Ger. Ps. 216824 and 216825) makes such solutions by acidulating solutions of thiosulphates in glycerine with addition of thickening agents, *e.g.* gelatine.

Sven Odén (*Z. Chem. Ind. Coll.*, 1911, p. 186) prepares colloid solutions of sulphur of various degrees of dispersion by fractional coagulation.

"Elastic india-rubber-like sulphur," according to Weimarn (*Chem. Ind.*, 1911, p. 398), is obtained by pouring melted sulphur, heated to 400°, in a thin jet into liquid air. It then forms thin strings of ½ to 1 mm. diameter, which at first are hard and fragile, but later on acquire such elasticity that they can be drawn out to 5·5 times the original length.

Raffo and Mancini (*Z. Chem. Ind. Coll.*, 1908, p. 358) obtain colloidal sulphur by pouring a concentrated solution of sodium thiosulphate into strong sulphuric acid, sp. gr. 1·84, kept cool, *not* vice versâ. Later on (*ibid.*, 1911, p. 58) they found that the stability of the colloidal solution is due to the presence of sulphuric acid and sodium sulphate. The colloidal solutions are coagulated by the solutions of salts of K, Na, Mg, Zn, Al and Cr.

Vermorel and Dantong (*Comptes rend.*, 1911, p. 194) render sulphur fit to be wetted by solutions of metallic salts by moistening 100 g. of sulphur with a solution of 200 g. oleic acid in 2 litres denatured alcohol and evaporating the alcohol.

Kelber and Schwarz (G. P. 245621) obtain colloidal sulphur by the action of SO_2 on H_2S in the presence of glutine.

Technical Analysis of Sulphur.

Cf. the tests for the degree of fineness, *suprà*, p. 47.

The ordinary *technical assay* of brimstone is performed by burning a weighed quantity, say 10 g., in a small porcelain capsule, and estimating the quantity of ash left behind. It is, however, advisable to estimate also the *moisture* for which purpose, in order to prevent any evaporation during grinding, an average sample of the unground or merely roughly-crushed material, weighing 100 g., is dried at 100° C. for some hours in an oven or water-bath

Macagno (*Chem. News*, xliii. p. 192) proposed the *direct estimation of sulphur* by means of its solubility in carbon disulphide.[1] Pfeiffer (*Z. anorg. Chem.*, xv. p. 194, and Lunge, *Chem. techn. Untersuchungs methoden*, i. p. 240) has reinvestigated this matter and given the following prescriptions for this method:—Shake a weighed sample of powdered sulphur with exactly four times the quantity of pure carbon disulphide, filter, reduce the temperature to 15° C., and ascertain the specific gravity of the solution. The following table (abridged from the original) shows the number of parts of sulphur dissolved by 100 parts by weight of CS_2 at 15° C. for various specific gravities found:—

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[1] F. B. Carpenter (*J. Soc. Chem. Ind.*, 1902, p. 832) points out that crude sulphur sometimes contains a large quantity of gypsum, which interferes with the carbon-disulphide treatment. In such cases the calcium sulphate must be previously removed by boiling with hydrochloric acid.

Specific gravity.	Sulphur dissolved.	Specific gravity	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.
1·2708	0	1·3087	8·5	1·3426	17·0
1·2731	0·5	1·3108	9·0	1·3445	17·5
1·2754	1·0	1·3129	9·5	1·3463	18·0
1·2779	1·5	1·3150	10·0	1·3481	18·5
1·2800	2·0	1·3170	10·5	1·3500	19·0
1·2833	2·5	1·3190	11·0	1·3517	19·5
1·2847	3·0	1·3211	11·5	1·3536	20·0
1·2870	3·5	1·3231	12·0	1·3553	20·5
1·2894	4·0	1·3251	12·5	1·3571	21·0
1·2916	4·5	1·3271	13·0	1·3587	21·5
1·2938	5·0	1·3291	13·5	1·3605	22·0
1·2960	5·5	1·3311	14·0	1·3622	22·5
1·2982	6·0	1·3330	14·5	1·3640	23·0
1·3003	6·5	1·3350	15·0	1·3657	23·5
1·3024	7·0	1·3369	15·5	1·3674	24·0
1·3045	7·5	1·3388	16·0	1·3692	24·5
1·3066	8·0	1·3408	16·5	1·3709	25·0

The same subject is again treated by P. Fuchs (*Z. angew. Chem.*, 1898, p. 1189). His figures are slightly different from those of Pfeiffer; but the latter's results (which were obtained in my own laboratory) seem to me the most accurate obtainable.

Ceruti (*Chem. Centr.*, 1904, p. 615) places 1 or 2 g. of the commercial sulphur on a filter, dried at 100° and weighed, gradually adds 50 c.c. of aniline (boiling-point 180° to 185°) heated to 120° to 130°, and collects the filtrate. The filter is washed with aniline, dried at 100° and reweighed, thus showing the amount of impurities insoluble in aniline. The filtrate is mixed with hydrochloric acid, allowed to cool, the precipitate then forming is washed on a weighed filter, dried in a vacuum over concentrated sulphuric acid, and thus the real S present is found.

W. N. Lévy (*Chem. Cbl.*, 1911, ii. p. 1883) employs the solubility of sulphur in carbon disulphide also for its estimation in sand, etc., containing it.

In *spent oxide of gas-works*, Davis and Foucar estimate the free sulphur by converting it into thiocyanate by means of an alcoholic solution of sodium cyanide, and titrating the thiocyanate with silver nitrate in the well-known manner (*J. Soc. Chem. Ind.*, 1912, p. 100).

Estimation of the Impurities of Sulphur—*Bituminous* substances are most easily recognised by the colour of the sulphur; they occur chiefly in sulphur made from spent oxide of gas-works, which is sometimes coloured quite black. Peratoner (*Chem. Cbl.*, 1909, ii. 479) found in ordinary crude Sicilian brimstone 0·03 to 2·44 per cent., but even in so-called "dark brimstone" not above 5 to 8 per cent. bitumen.

Arsenic sometimes occurs in brimstone, more especially in that recovered from alkali-works, always in the shape of arsenious sulphide. On extracting the brimstone with disulphide of carbon, the As_2S_3 remains behind and can be estimated. Schäppi (*Chem. Ind.*, 1881, p. 409) prefers extracting the As_2S_3 with dilute ammonia (as described by the German Pharmacopœia) at 70° or 80° C. From this solution the sulphur can be precipitated with silver nitrate as Ag_2S, which is filtered, washed, dissolved in hot nitric acid, and estimated as chloride; 6 molecules of AgCl correspond to 1 of As_2S_3. It is, however, more expeditious to work volumetrically. The ammoniacal solution of arsenious sulphide is exactly neutralised with pure nitric acid, strongly diluted and titrated with decinormal silver nitrate, till a drop of the solution, on addition of neutral potassium chromate, produces a brown colour. When employing 10 g. of sulphur for extraction with ammonia, each cubic centimetre of decinormal silver solution indicates 0·041 per cent. As_2S_3. Sometimes arsenic occurs in recovered sulphur in the shape of ferric or calcium arsenite, which cannot be found by the above process, but only by extracting the sulphur with carbon disulphide and digesting the residue with aqua regia.

A qualitative reaction for arsenic consists in agitating 1 g. sulphur with 15 drops liquor ammonia and 2 c.c. water for half an hour, filtering, adding to the filtrate 30 drops of hydrochloric acid and 15 drops solution of oxalic acid, placing a bright piece of brass in the solution and heating to 60° to 100°; in the presence of arsenic the brass is stained grey or black (Hager, *Pharm. Centr.*, 1884, pp. 263 and 443).

Steel (*Chem. News*, vol. lxxxvi. p. 135) declares the method of Schäppi for the detection of arsenic in sulphur to be erroneous. He proceeds as follows:—He extracts 200 g. of the sample during two hours in a paper filter in the Soxhlet apparatus with carbon disulphide, withdraws the paper filter, allows the CS_2 to evaporate, scrapes out the residue, heats this with 50 c.c. strong nitric acid till all acid is driven off, adds 1 c.c. strong hydrochloric acid and, after a few minutes, 5 c.c. warm water, filters into a test-tube, washes the insoluble residue with a little water, adds to the solution 20 c.c. strong hydrochloric acid, 1 or 2 c.c. of a fairly concentrated solution of stannous chloride in hydrochloric acid, and, lastly, 3 c.c. of strong sulphuric acid, heats gently and allows to stand over-night. If As or Se (insoluble in CS_2) is present, a dark brown precipitate is formed. This is filtered through asbestos (purified by aqua regia), washed and dried at 100°, transferred to a hard glass tube, 7 mm. bore closed at one end; the tube is then drawn out immediately above the contents to 1·5 mm. bore for a length of about 80 mm. The bulb portion, containing the asbestos, etc., is heated to redness in a Bunsen flame. As and Se are driven off and condense in the narrow part of the tube. Se appears both in the black and red modification and is at once identified by its characteristic odour; As is found by heating the sublimate in a current of air, when As_2O_3 forms a ring of glistening crystals, or, in the presence of traces of water, globules of a solution of oxide. If no selenium is found here, it may be sought for in the CS_2 solution, by distilling off the CS_2, oxidising the mass of sulphur by means of fuming nitric acid [no mean task with 200 g. sulphur!], filtering through asbestos, evaporating the filtrate till strong white fumes of sulphuric acid appear, and then reducing with $SnCl_2$, etc., as above.

Brand (*Chem. Cbl.*, 1908, p. 762) prefers the method of Gutscheid, which he carries out as follows. He digests 5 g. sulphur, etc., with 25 dilute ammoniacal liquor (1 : 3) during a quarter of an hour, filters, washes the filter with a little water, evaporates the solution to dryness, pours a few drops of nitric acid over the residue, dries in a porcelain dish, dissolves in 8 to 10 c.c. dilute sulphuric acid, pours into a large test-tube, containing a few pieces of pure zinc, puts a loose plug of cotton-wool into the neck of the tube, and on this a piece of filter-paper, moistened with a drop of concentrated silver-nitrate solution (1 : 1). The moistened spot is coloured lemon yellow, more or less quickly, according to the quantity of arsenic present, and on addition of water turns black. In the case of brimstone rolls, intended for sulphurising hops, no sensible coloration ought to take place within a quarter of an hour. He suggests testing by this method all samples of sulphur intended for preserving articles of food.

Apart from the already described methods, *selenium* is also discovered by deflagrating the sulphur with nitrate of potash, dissolving in hydrochloric acid, and treating with SO_2, which precipitates the selenium as a red powder.

Reed (*Chem. Zeit. Rep.*, 1897, p. 252) describes the American test for selenium. Boil 0·5 g. sulphur with a solution of 0·5 g. potassium cyanide in 5 c.c. water, filter and acidify the filtrate with HCl; a red colour, appearing within an hour, shows selenium. Or else boil 1 g. sulphur with a solution of 2 g. potassium cyanide for an hour, add another 0·5 g. KCy and boil for another half-hour. Of course any iron present will react with the sulphocyanide formed.

Klason (*Chem. Zeit.*, 1911, p. 1345; *J. Chem. Soc. Abstr.*, 1912, ii. p. 201; fully in *Z. angew. Chem.*, 1912, pp. 514 *et seq.*) states that already 0·5 mg. selenium per litre makes sulphuric acid useless for the treatment of materials in paper-making. Such small quantities can be estimated by the action of hydriodic acid which by the action of selenious acid is decomposed, iodine being set free and found by means of starch solution. This method is applicable to the examination of brimstone as well as of pyrites. Sicilian brimstone contains about 0·9 g. Se, Japanese brimstone 1 to 20 g. Se per ton. The selenium passes over partly into the burner gases and partly into the cinders. The higher the temperature, the more Se passes into the burner gases, but the cinders contain at least 30 per cent. of the total selenium, and in the case of cupreous pyrites more than that. Falun pyrites contains on an average 10 g. Se per ton, but sometimes three or four times as much. By his hydriodic process Klason was able to find 92 per cent. of the selenium in the boiling acid, even with quantities of 0·25 mg. per litre.

Durier (*Ann. falsif.*, xxxvii. 584; *Abstr. Amer. Chem. Soc.*, 1912, 535) describes an adulterant employed for ground sulphur, consisting of infusorial earth, which can be easily detected by chemical or microscopical methods. It contains about 75 per cent. silica, and yields at least 80 per cent. ash. As sulphur contains at most 2 per cent. ash, its incineration will reveal the adulteration; also microscopical examination of the original material or the ash, which shows the presence of diatoms.

Analysis of Refined Sulphur.—Sulphur in blocks or rolls is almost always practically pure; it may be tested for ashes, arsenic, and selenium as above.

Flowers of Sulphur is never quite pure unless specially washed; it always contains some acid. Ianda (*Fischer's Jahresber.*, 1898, p. 421) found up to 0·283 per cent. ashes; the average of thirty samples was 0·063 per cent. He also tests the solubility in boiling solution of caustic soda of sp. gr. 1·2. This varied from 88 per cent. (in one case 68 per cent.) to 99·99 per cent., average 98·04 per cent.

Domergue (*Chem. Zeit. Rep.*, 1905, p. 19) acknowledges only such an article as "flowers of Sulphur" which contains at least 25 per cent. of sulphur insoluble in carbon disulphide. Heckel (*Chem. Centr.*, 1905, i. p. 205) agrees to this. But the French Agricultural Society (*ibid.*, 1905, ii., p. 1482) is of different opinion. On the one hand, the percentage of sulphur insoluble in CS_2 in flowers of sulphur gradually decreases on keeping, and may sink from 30 or 35 per cent. to 12 per cent., without being less efficacious against the disease of the vine. On the other hand, mixtures of sublimed sulphur and ground sulphur, containing but 13 to 15 per cent. insoluble in CS_2, would pass as the proper article for the vine grower, although they are not so. Domergue (*Chem. Centr.*, 1906, i. p. 8) replies that he asked merely for a *minimum* of 12 per cent. S insoluble in CS_2 in unadulterated flowers of sulphur, but an excess over that proportion is admissible.

Marcille (*Ann. Chim. appl.*, x. p. 101; *Z. angew. Chem.*, 1906, p. 99) tests the commercial value of sublimed sulphur by shaking up 5 g. in a Chancel tube with carbon disulphide free from water and reading off the volume of the insoluble matter on the division of the tube; the Chancel degrees answer pretty nearly to the percentage of S insoluble in CS_2.

Taurel and Griffet (*Comptes rend.*, clii. p. 1182; *J. Soc. Chem. Ind.*, 1911, p. 683) treat commercial mixtures of sublimed sulphur and other forms of sulphur with carbon bisulphide, which dissolves the ground or precipitated sulphur, whilst the amorphous coatings of the sublimed sulphur globules (which constitute from 12 to 33 per cent. of the sublimed sulphur) remain insoluble; they retain their form and the apparent volume of the sublimed sulphur is not altered. Weigh 15 g. of the sample into each of two graduated tubes of equal diameter; previously 35 c.c. petroleum spirit had been put into one, and 35 c.c. of CS_2 into the other tube. Shake gently and submit both tubes to centrifugal action. The volume of the sediment in the CS_2 tube gives the volume of the sublimed sulphur present, the volume in the other tube showing the total volume of the mixed sulphurs.

2. PYRITES.[1]

What is called *pyrites* or *iron-pyrites*, in a technical sense, is hardly ever pure iron disulphide, FeS_2, but either a mixture of this with gangue, or more frequently at the same time with other sulphuretted ores, as shown by numerous analyses. The iron disulphide may be present either as iron-pyrites proper or as marcasite. The *iron-pyrites proper* crystallises in the regular system, with parallel hemihedry, proved even on the faces of the cube by striation (Fig. 4).

Besides the cube, Fig. 4 (I), the octahedron, *a* (II), is frequently found, often modified by the pyritohedron, *b* (III), and, if both are equally developed, forming the icosahedron (II). The combined forms IV, V, VI, as well as twin crystals, frequently occur. The crystals are often well developed; but in the pyrites used on the large scale they are mostly quite indistinct. The colour of pure pyrites is greyish yellow, and easily distinguished from that of copper-pyrites. The microcrystalline pyrites of trade often shows other colours, even a slate-grey; the powder is brownish black. Its cleavage parallel to the faces of the cube is not very pronounced; the fracture is conchoidal or irregular. Hardness 6 to 6½, sp. gr. 4·83 to 5·2. Pure FeS_2 contains 46·58 per cent. of iron and 53·42 per cent. of sulphur.

According to Mène, the pyrites from volcanic formations contains no water, but that from sedimentary strata both water and clay. Among the first he classes the yellow octahedral pyrites, which is stable in the air; among the latter the grey cubical pyrites, which is easily transformed into ferric sulphate (*Comptes rend.*, 29th April 1867). Some descriptions of pyrites, in consequence of their content of water, on roasting fly asunder

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[1] A very complete treatise on pyrites has been published in 1907 by P. Truchot: *Les Pyrites, Pyrites de Fer, Pyrites de Cuivre*, Paris, chez Dunod et Pinat.

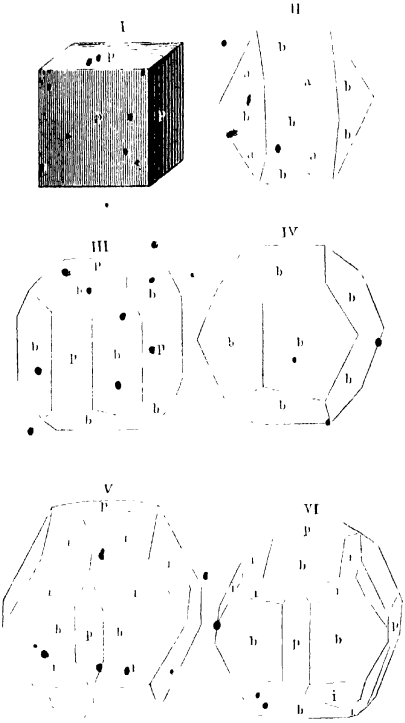
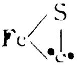


FIG. 4.

with the force of an explosion; this is by Klason (*Chem. Zeit.*, 1911, p. 1334) attributed to the presence of zeolites.

According to G. W. Plummer (*J. Amer. Chem. Soc.*, 1911, xxxiii. pp. 1487 *et seq.*), the behaviour of marcasite and pyrites towards bismuth chloride proves that both minerals contain their iron wholly in the ferrous state, and that their formula must hence be:


$\mathrm{Fe}\begin{array}{l}\diagup \mathrm{S}\\ \quad |\\ \diagdown \mathrm{S}\end{array}$

Feld (*Z. angew. Chem.*, 1910, p. 971), on the strength of experiments, explains the formation of the natural pyrites beds by the action of thiosulphate, in the presence of hydrogen sulphide, on FeS and S. Only a very small quantity of thiosulphate need be present if the conditions are favourable for its continuous reformation.

Marcasite crystallises in the rhombic system, in rhombical prisms $m = 106° 2'$ with longitudinal faces $l = 100°$ and r, and the end face p inclined to r at an angle of 158° 20′. It frequently occurs in twin crystals, partially united along one of the faces m, also in triplets and quadruplets, etc. (Fig. 5), in fibrous, bulbous, etc., varieties; cleavage indistinct; hardness 6 to 6·5; sp. gr. 4·65 to 4·88; colour grey to yellow or greenish yellow, lighter than iron-pyrites proper; powder greenish dark grey. Marcasite is most frequently found in bituminous slate and coal, and decomposes even more quickly than pyrites, with the formation of ferrous sulphate and basic ferric sulphate.

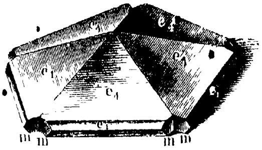


FIG. 5.

Detailed investigations on the different behaviour of pyrites and marcasite have been published by A. P. Brown (*Chem. News*, 1895, lxxi. p. 139, and following numbers) and by Stokes (*Bulletin U.S. Geol. Surv.*, No. 186, 1901) and Oknow (*Metallurgie*, viii. p. 539).

In the ores of commerce there is often present, mixed with FeS_2, *magnetic pyrites* (*pyrrhotite*) of the formula Fe_7S_8, with 60·5 iron and 39·5 sulphur; colour between brass-yellow and copper-red; hardness 3·5 to 4·5; sp. gr. 4·4 to 4·7. Pyrrhotite occurs by itself in large quantities, which have been scarcely utilised up to the present, but according to Sjöstedt (*Rev. Amer. Chem. Research*, 1904, p. 305), Sudbury pyrrhotite containing 15 to 20 per cent. sulphur has been successfully roasted, with auxiliary heat, in a powdered form by means of a modified Herreshoff furnace, for the manufacture of sulphite pulp, of liquid sulphur dioxide, and of sulphuric acid. In *Eng. and Min. J.*, lxxviii. 697, this is also reported about pyrrhotite from Pulaski (Va), with 28 per cent. S and 3 per cent. Ni, but it is not stated whether this use has been found to answer in the long run.

The *copper-pyrites* so often mixed with iron-pyrites is distinguished from it by its colour, yellow as brass, sometimes as gold; this colour modifies that of the iron-pyrites according to the degree of admixture. It crystallises in the tetragonal system, but in the ores which concern us always occurs in a microcrystalline form. Its hardness is 3·5 to 4·0, sp. gr. 4·1 to 4·3. Pure copper-pyrites of the formula $FeCuS_2$ should contain 30·53 per cent. iron, 34·58 per cent. copper, and 34·88 per cent. sulphur; but the ores serving for the manufacture of sulphuric acid rarely contain beyond 4 per cent. of copper.

An investigation of the *calorific value* of pyrites has been made by Somermeier (*J. Amer. Chem. Soc.*, 1904, xxvi. pp. 555 *et seq.*). He sums up his conclusion (on p. 566 of his paper) as follows. For pure pyrites (53·2 per cent. S) the calorific value of the sulphur contained therein is 4957 cal. per gramme in the calorimeter, where $Fe_3O_4+6SO_3$ aq are formed, but only 2915 cal. per gramme of sulphur on burning in the air under ordinary circumstances where $Fe_2O_3+4SO_2$ is formed. From this we may calculate the calorific value per gramme of pyrites = 1557 cal. [This determination and calculations cannot be considered as quite exact, but only as approximately correct.]

The first application of pyrites for sulphuric-acid making is generally ascribed to a Mr Hill, of Deptford, who in 1818 took out a patent for it.[1] In France, Clément-Desormes seems to have made the first proposals and experiments in that way. His trials did not, however, succeed, because he believed it necessary to increase the combustibility of pyrites by an addition of coal. This is both unnecessary, with properly constructed kilns, and very injurious to the process, owing to the detrimental action of the carbon dioxide getting into the chambers. A great difficulty was experienced in lighting the kilns. So long as it was attempted to do this from below, like an ordinary fire, the thing would not work. According to a communication from Mr Todd (Government Inspector of Alkali Works), a workman of his father's in Cornwall, in 1830, accidentally discovered the way of lighting the kilns from the top, such as is practised to this day. Generally, however, the principal merit of introducing pyrites is ascribed to Messrs Perret and Son, of Chessy, who were led to it by the necessity of desulphurising their cupreous pyrites previously to getting the copper, and of condensing the gas evolved. There was no question then of supplanting the Sicilian sulphur generally. Perret and Son, with the greatest care, inquired into all the conditions necessary for a proper combustion of the ore; and to them the honour is due of having overcome all the difficulties opposed to the solution of this problem, and of having rendered the process technically useful. Already in 1833 they had burnt iron-pyrites successfully; and in a patent dated 20th November 1835 they described their process, to which their partner, Olivier, is said to have given the first impulse. In 1837, Messrs Wehrle and Braun, in Bohemia, used pyrites for generating sulphurous acid (Otto, *Lehrbuch der Chemie*, 4th ed. iii 1, p. 545); but, according to Bauer (*loc. cit.*, p. 6), I. Brem had introduced this process into Austria (at Lukawetz) already in 1833—that is, at the same time as Perret.

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[1] Sorel attributes this honour to his countryman, d'Artigues, in 1793.

These trials at making sulphuric acid from pyrites possessed, however, only local interest; and probably for a long time no general attempt to do away with Sicilian brimstone would have been made, but for the Neapolitan Government, in 1838, being induced to grant a monopoly for the exportation of Sicilian sulphur to the Marseilles firm of Taix and Co. This firm at once raised the price of brimstone from £5 to £14 per ton, and thus would have given a fatal blow to the manufacture of artificial soda-ash, just then beginning to take a firm hold, if no other source of sulphur had been known, and if such an unnatural measure could have been carried out at all. But the attempt came too late—just after Perret and Son had proved that the pyrites occurring in most industrial countries may be used for vitriol-making without any difficulty. The result was to be foreseen. Once the discovery of a new source of sulphur had become a matter of necessity, there were, within twelve months from the rise in the price of brimstone, fifteen patents taken out in England for burning pyrites for the purpose of making sulphurous acid, and even a larger number for making sulphur from pyrites, gypsum, etc.

According to Muspratt's *Chemistry* (vol ii. p. 1023), Dr Thomas Thomson was the first in England to point to pyrites in this crisis; but most probably many others at the same time turned to it. So much is proved—that Thomas Farmer, of London, was the first in England who employed pyrites on a large scale (in 1839) for the manufacture of sulphuric acid (Hofman, *Report by the Juries*, International Exhibition, 1862, Class II., Section A, p. 12).

Mr E. K. Muspratt states that his father, in 1839 and 1840, used large quantities of Wicklow and Welsh pyrites at Liverpool and Newton, the cupreous cinders being sent to the Sutton Copper Company at St Helens.

In Germany the Oker works, at the Rammelsberg, near Goslar, seem to have been the first who calcined the local ore in such a way as to convert the sulphur dioxide given off into sulphuric acid in acid-chambers; and other smelting-works, such as those at Freiberg, followed their example. In these cases the reasons were, not only that at a comparatively small expense sulphuric acid could be obtained as a by-product from the sulphur dioxide otherwise lost, but also that the acid fumes destroyed the vegetation of a large district round the works, and that means had to be taken for preventing this, apart from any consideration of profit.

The Sicilian brimstone monopoly certainly did not last long; diplomatic pressure on the part of England soon led to its abolition; and with the lowering of the price of brimstone most works at first returned to its employment. But the ice was now broken; the conviction had been gained that it was possible to make acid without Sicilian brimstone; the owners of pyrites-mines took pains to advance the use of pyrites by low prices; and thus, in the course of the next twenty years, brimstone was gradually, but steadily, driven from its place in sulphuric-acid making, in proportion as, on the one hand, it became dearer from the causes above mentioned (disease of the vines, etc.), and as more pyrites-mines were opened out. In 1852 brimstone was no longer used in Lancashire, but on the Tyne 7580 tons of it were still burned. About 1860 or a little after this process ceased, and since that time no alkali has been manufactured in Great Britain with the employment of brimstone, although the latter, as we shall see later on, is employed a good deal even now for the manufacture of sulphuric acid in that country.

The decisive point in favour of the use of pyrites was this, that continually increasing quantities of *cupriferous iron-pyrites* came into the market, from Spain especially (first in 1859), but also from other countries. These had in any case to be burned and their sulphur expelled before they could be worked for copper. Already with Perret and Son this had been the stimulus for their efforts; but the use of such pyrites has increased on a colossal scale in consequence of the opening out of the cupreous-pyrites mines in the South of Spain, in Portugal, and in Norway. In England non-cupreous iron-pyrites is now all but out of the field, and has been supplanted by cupreous pyrites. This has been the case to a less extent in France and Germany, because they possess mines of rich iron-pyrites, which in England are not numerous; but even in those countries more cupreous pyrites is now used. In 1867 pyrites had almost entirely supplanted brimstone in France as a raw material for acid-making in the large industrial centres (*Rapport du Jury International, Expos. Univ. de* 1867, vol. vii. p. 19). In Germany this state was brought about somewhat later, but quite as completely. Only during the years 1871 to 1873, when the price of pyrites had risen very high, a few factories in Hanover, in Hamburg, and Stettin temporarily returned to the use of brimstone (Hasenclever, *loc. cit.* p. 155); but with the lowering of the prices of pyrites this was given up again. Spanish pyrites began to be used in Germany in 1877.

Thus, starting from the use of ordinary iron-pyrites, that of cupriferous iron-pyrites has followed; and to this was added the employment of other sulphurous ores and of the intermediate products of smelting—for instance, copper-regulus ("coarse metal") at Mansfield and Swansea. The first chambers working with SO_2 from the metallurgical treatment of copper and lead ores were started at Oker in 1859, at Freiberg in 1861. The Freiberg works employ for this purpose even poor lead-matts with about 22 per cent. of sulphur, which formerly was thought impossible (Bode, *Beitrage zur Theorie und Praxis der Schwefelsaurefabrikation*, 1872, p. 1). We shall further on describe the application of other sulphur-ores apart from pyrites proper.

The *principal sources of pyrites* will now be enumerated without separating the cupreous from the non-cupreous, because no strict limit can be drawn. Some kinds of pyrites contain so little copper (below 1 per cent.) that it cannot be utilised; and these go with the totally non-cupreous ores.

Great Britain possesses several deposits of pyrites, but none of very great importance. In Cornwall and Devonshire pyrites of the following composition is found:—

	Pattinson.		Clapham (8 analyses).
Sulphur	27·00		24·013 to 34·880
Iron	22·69		27·076 „ 60·676
Copper	2·00		0·400 „ 4·600
Lead	trace		0· „ 7·446
Zinc	1·23		0· „ 9·086
Lime	0·22	Gypsum	0· „ 0·596
Carbonate of Lime	...		0· „ 3·579
Magnesia	0·12		...
Arsenic	0·32		0· „ 1·160
Insoluble (silica)	45·60		2·000 „ 38·676
Oxygen as Fe_2O_3	0·13		...
Moisture	0·64		...
	99·95		

Cleveland pyrites (from the North of Yorkshire) is only used in a local factory; in 1874, 500 tons of it were obtained. Composition (according to Pattinson's analysis):—

Iron disulphide (corresponding to 27·18 sulphur)	52·12
Iron protoxide	11·92
Alumina	8·10
Lime	0·27
Magnesia	1·00
Carbonic acid	2·40
Insoluble in acid	11·12
Water	12·86
	99·79

In *Ireland* there are large beds of pyrites, especially in the county of Wicklow; and up to about 1862 this Irish ore supplied a very large portion of the pyrites used in England. In 1860 still 40,000 tons of it were imported into the Tyne River; but in 1863 the importation had fallen to 4000 tons, and has long since ceased entirely. The same has been the case in Lancashire; and only a few works in Ireland itself burn this kind of pyrites. It is found in the county of Wicklow in beds from 6 to 50 ft. in thickness, which overlie siliceous clay-slate. The beds go down to depths of 80 to 100 fathoms. The bulk of the ore contains only 30 to 35 per cent. of sulphur. A small quantity only of richer ore (analyses *a*, *b*, *c*) has been found in the valley of Ovoca. The Irish ore is too hard and slaty and does not burn well; it requires a great heat, and consequently deep kilns. It nearly always contains copper but rarely sufficient to pay for extracting it, from which standpoint the following analyses must be judged:—

	Pattinson.	Clapham.			
	a.	*b.*	*c.*	*d.*	*e.*
Sulphur	44·20	40·410	42·128	37·975	34·676
Iron	40·52	32·222	35·000	34·650	42·400
Copper	0·90	4·133	2·400	2·400	1·333
Lead	1·50	2·963	1·600	1·080	1·593
Zinc	3·51	...		...	...
Arsenic	0·33	...	0·602	0·400	0·183
Lime	0·24	...	...	...	...
Insoluble	8·80	17·676	18·696	22·500	20·000
Moisture	0·09	...	...	...	...
Oxygen as Fe_2O_3	0·25	...	...	...	...
	100·34	97·404	100·406	99·005	100·185

In *Wales* (in the Cae Coch Mine) pyrites is found entirely free from arsenic, according to Drinkwater (*J. Soc. Chem. Ind.*, 1885, p. 533). It contains 48·3 per cent. of sulphur, and is used for manufacturing very pure oil of vitriol.

A certain quantity of pyrites is picked from coals, and is known as *coal-brasses*. If quite free from coal, they are very rich—according to R. D. Thompson (in Richardson & Watts's *Chemical Technology*, vol. i. pt. iii. p. 15), 53·55 sulphur, 45·07 iron, 0·70 manganese, 0·80 silica; but practically they cannot be obtained in this state, and the carbonaceous matter adhering to them causes very much trouble in the vitriol chambers. Their principal use in acid-making is for lighting the burners, or for getting up their heat if it has gone down. Mr G. E. Davis informs me that coal-brasses with 44 per cent. S and some carbon can be burnt in ordinary pyrites-kilns, and, if proper arrangements are made, yield perfectly clear acid from the Glover tower. Apart from this they are worked up by weathering for copperas and Venetian red, and this is probably the way in which most of the quantity obtained in England (10,000 tons in 1874) is consumed.

The total production of pyrites in the United Kingdom was 25,401 tons in 1885; 27,829 tons in 1886; in 1887, 22,079 tons; in 1888, 23,507 tons; in 1889, 17,719 tons; in 1890, 16,018 tons; 1895, 9193 tons; 1896, 10,177 tons; 1897, 10,752 tons; 1898, 12,302 tons; 1899, 12,426 tons; 1900, 12,484 tons; 1901, 10,238 tons; 1902, 9168 tons; 1903, 9639 tons; 1904, 10,287 tons; 1905, 12,186 tons; 1906, 11,140 tons; 1907, 10,194 tons; 1908, 9448 tons; 1909, 8429 tons.

The *importations of foreign pyrites* into Great Britain during the years 1862 to 1887 are quoted in our second edition, Vol. I. p. 32; those of the years 1888 to 1900 in our third edition, Vol. I. p. 42. Here we shall give the figures for the years 1906 to 1910 from the Bluebook (Annual Statement of the Trade, etc.) for 1910. The figures denote tons of iron and copper pyrites:—

Imported from	1906	1907.	1908.	1909.	1910.
Sweden	9,999	7,561	506	685	...
Norway	64,530	70,288	66,767	79,168	90,935
France	21,560	19,255	15,190	35,149	47,522
Portugal	55,907	84,622	73,342	78,966	79,383
Spain	566,455	566,166	563,906	540,485	537,972
Italy	2,676	...	6,550	16,980	10,001
Venezuela . . .	...	...	1,300	1,100	...
Chili	3,271	...	4,912	986	...
Other foreign countries .	5,906	1,905	2,704	4,998	7,346
Total from foreign countries	730,364	749,818	735,177	758,517	773,159
,, British possessions	28,960	19,323	23,733	32,551	39,088
Total . .	759,324	769,141	758,910	791,068	812,247

The exportation of pyrites from the United Kingdom is practically nothing.

The most important *German* pyrites-bed is that of *Meggen* in the Siegen district, in Westphalia, 3 miles from the Altenhunden station on the Ruhr-Sieg railway. This bed occurs along with heavy spar in the so-called "Kramenzel"; it is known for a length of 2000 fathoms, and its thickness changes from ¾ to 3 fathoms (Wagner's *Jahresber.*, 1865, p. 221). The same authority states it to be "grey iron-pyrites," quite uncrystalline, free from arsenic [?]. The mass of ore above the bottom of the valley is estimated at 4½ million tons; how far the ore descends below the bottom of the valley is as yet unknown.

The ore has not an attractive outward appearance; its colour is slate-grey; but it burns very well in the kilns, and it would be even more valuable if the zinc contained in it did not prevent its burning completely. Older analyses of it are given in our second edition, Vol. I. p. 35. Here I quote more recent analyses made at the Rhenania Chemical Works, as furnished to me by Dr R. Hasenclever in 1902:—

	a	*b*	Average.
Gangue . . .	12·02	12·96	12·0
Sulphur . . .	41·94	43·42	40·0 to 43·0
Iron	34·92	35·56	35·0
Zinc	7·56	5·81	7·0
Lead	0·38	not estimated	0·3 to 0·5
Lime . . .	0·50	,,	0·1 ,, 0·5
Arsenic. . . .	trace	0·05	trace ,, 0·05
Total . .	97·32	97·80	...

The average represents 12 per cent. gangue, 75 per cent. iron-pyrites (FeS_2), 10·5 per cent. zinc-blende (ZnS), together 97·5.

Jurisch (*Schwefelsaurefabrikation*, pp. 14 *et seq.*) quotes a number of analyses of Westphalian pyrites, by F. Quincke, for the year 1892. In these the sulphur varied from 41 to 46·75 per cent., iron from 29·55 to 36·16 per cent., zinc from 8·2 to 19·41 per cent. (I exclude two samples containing 27·58 and 42·05 per cent. zinc, which are more correctly classed as blende than as pyrites), lead from 0·3 to 1·7 per cent., arsenic from 0·1 to 0·2 per cent., besides silica, alumina, lime, magnesia, manganese, alkalies, and small quantities of other substances.

The same source quotes analyses of pyrites from Bensberg (46·86 per cent. S), Aachen (46·0 per cent.), Rammelsberg (44·65 to 48·4 per cent.), Freiberg (52·20 per cent.).

The following is a complete analysis by Fresenius of ore from the Philippine pit belonging to the Sicilia Mining Company at Meggen, made in 1898:—

Iron	34·89
Zinc	8·38
Manganese	0·155
Cobalt and Nickel	0·024
Lead	0·298
Alumina	trace
Lime	1·41
Magnesia	0·75
Sulphur	44·55
Arsenic	0·07
Carbon dioxide	1·90
Phosphorus peroxide	trace
Gangue	5·83
Oxygen as Sulphate, Thiosulphate, etc., and traces of other substances	1·743
	100·000

There are smaller beds of pyrites in several other places in Germany, such as those near Goslar, near Schwelm in Westphalia, near Merzdorf in Silesia, etc. Their production is only small compared with that of the Meggen pyrites. The pyrites of the Rammelsberg in the Harz, according to Mène, contains 48·4 per cent. of sulphur (probably only picked lumps). The cupreous pyrites of the same place is stated by Hilgenfeld to contain:—

Copper	12·22
Lead	2·43
Iron	39·10
Zinc, Manganese, Cobalt, Nickel	1·23
Arsenic	0·18
Antimony	0·16
Sulphur	44·65
Selenium, Thallium, Indium, Bismuth	traces
	99·97

The bed of Schwelm in Westphalia, in the Devonian formation, has a thickness of from 10 to 33 ft., over a surface of nearly 150 acres, and is covered by rich iron-ore; the pyrites itself consists of two-thirds powder mixed with well-crystallised pieces. The ore contains about 40 per cent. sulphur, and more or less clay, which is removed by washing; after this it is sold to the vitriol-makers, who like it on account of its freedom from arsenic (*Dingl. polyt. J.*, ccxxviii. p. 283); Hjelt, however, found more arsenic in it than in Meggen pyrites.

On the island of Wollin a pyrites-bed is found in a bed of marl belonging to the chalk formation.

A great drawback to the German ores is the presence of zinc, which retains a considerable quantity of sulphur in the state of sulphate. In Silesia 14 per cent. of zinc is allowed as a maximum; upwards of this for each per cent. of zinc the same quantity of sulphur is deducted from the invoice (Kosmann, in *Fischer's Jahresber.*, 1886, p. 268).

The production of German pyrites during the years 1853 to 1886 is quoted in the second edition of this work, Vol. I. p. 38; that between 1891 and 1897 by Hasenclever, *Chem. Ind.*, 1899, p. 25. The maximum production in 1874 was 143,476 tons; the average of those ten years is about 130,000 tons. The production was 133,302 tons in 1897, 136,849 tons in 1898, 144,602 tons in 1899, 170,867 tons in 1903, 174,782 tons in 1904, 185,368 tons in 1905, 196,571 tons in 1906, 196,320 tons in 1907, 196,971 tons in 1908, 198,688 tons in 1909, and 215,700 tons in 1910. The importation of foreign (chiefly Spanish) pyrites into Germany increased from 238,643 tons in 1891 to 357,017 tons in 1897, all of this for sulphuric acid. In 1898 it was 376,817 tons; in 1899, 437,732 tons; in 1900, 457,679 tons; in 1901, 488,632 tons in 1902, 482,095 tons; in 1908, 643,487 tons; in 1909, 679,647 tons; in 1910, 792,000 tons.

The exportation is small: in 1898, 19,219 tons; in 1899, 16,985 tons; in 1900, 24,936 tons; in 1901, 23,680 tons; in 1902, 35,370 tons.

Austria - Hungary possesses large beds of pyrites at Schemnitz and Schmolnitz in Hungary, in Styria, and Tyrol. The pyrites from Schemnitz contains on an average 47 to 48 per cent. S, 39 to 40 per cent. Fe, 0·58 per cent. Cu, 1·5 to 2 per cent. Zn, besides lead, silver (81 g. per ton), and gold (2·2 g. per ton). Schmölnitz ore contains 44 to 48 per cent. S, 0·4 to 0·6 per cent. Cu, 2 to 3 per cent. Zn. Jurisch (from whose *Schwefelsäure-fabrikation*, p. 18, the above is taken) quotes an analysis of Schmölnitz pyrites with 48·89 per cent. S, 0·32 per cent. Cu, 0·14 per cent. As; 70,000 or 80,000 tons of this pyrites are obtained per annum.

At Davidsthal, in Bohemia, pyrites is found containing 49 per cent. of S with 6 per cent. carbon. It is used for manufacturing SO_3 by the contact process.

In Tyrol pyrites is found testing 40·5 to 41·3 per cent. S.

In Styria (Riedl, *Zeitschr. f. d. chem. Grossgewerbe*, ii. p. 567); in the Saun valley, a number of beds of very pure but easily decomposable pyrites occur in the clay porphyry, with a percentage of 48 to 52 of sulphur. It is used in the chemical works at Hrastnigg and in Bohemia. The production is about 3000 tons per annum (*Fischer's Jahresber.*, 1886, p. 255).

In *Switzerland*, in the Canton of Wallis, a pyrites is obtained which does not seem to have found any technical application as yet. Its composition, according to an analysis made in my laboratory, is:—

Sulphur	50·46
(of this 0·05 as lead sulphate in the insoluble residue)	
Iron	44·55
Lead	0·37
Lime	1·13
Magnesia	0·11
Carbonic acid	1·01
Silica, Iron peroxide, Alumina (insoluble)	1·70
Moisture	0·40
	99·73

In *Poland* pyrites occurs together with blende, containing some thallium (Antiporo, *Fischer's Jahresber.*, 1897, p. 421).

In *Belgium* a rich pyrites is met with, the great friability and softness of which do not tell in its favour. The following are analyses of this pyrites:—

	a	*b.*	*c.*	*d.*	*e*	*f.*
Sulphur	42·80	35·50	46·20	45·01	50·00	45·60
Iron	36·70	38·60	40·50	39·68	43·61	38·52
Ferric oxide	7·23	4·24	2·29	...	...	...
Oxygen in ferric oxide	...	...	...	0·32	0·18	6·00
Lead	0·92	0·65	0·41	0·37	...	...
Zinc	0·40	5·26	0·22	1·80	1·75	...
Arsenic	0·20	0·31	0·41	trace	trace	trace
Thallium	...	...	...	trace	...	...
Alumina	trace	...	...	...	...	...
Silica	8·86	14·90	9·10	12·23	2·85	9·00
Carbonic acid	...	...	...	...	0·73	...
Calcium carbonate	0·84	*trace*	...	...	...	0·11
Lime	...	...	...	0·25	0·92	...
Water	1·46	0·56	0·18	0·25	0·19	0·36
Total	99·41	100·02	99·46	99·91	100·14	99·59

(*a*, *b*, and *c* by Clapham in Richardson and Watt's *Chemical Technology*, vol. i. part iii. p. 14; *d*, pyrites from Rodieux near Spa; *e*, from Santon's pit on the Meuse, both by Pattinson, *loc. cit.*; *f*, by MacCulloch, *Chem. News*, xxvii. p. 125).

The Belgian pyrites is usually only got as a by-product in obtaining lead- and zinc-ores in the provinces of Liège and Namur; it is either microcrystalline or crystalline, or in bulbous pieces with a concentrically fibrous structure. Its quality varies very much. It is mostly used locally and in the north of France.

In 1860 as much as 42,513 tons of pyrites was got, but this was the maximum attained. In 1879 still 15,577 tons were procured, but in 1880 only 7913 tons, and in 1881, 2965 tons. The production remained about 2000 or 3000 tons for a number of years, but since 1898 it has been altogether insignificant.

In *France* the principal deposits of pyrites are those of the Rhone (Chessy and Sain-Bel) and of the South (Gard and Ardèche). The Rhone beds exist on both banks of the Brevenne, a tributary of the Saone, on a width of 4 or 5 miles. The bed on the left bank is that of Chessy, about 6 miles long and several yards thick. This pyrites is bright yellow, very crystalline and friable. When first got it contained 4 or 5 per cent. of copper; but the cupreous vein has run out, and the non-cupreous ore on this side has nearly ceased to be worked. The beds on the right bank are those of Sain-Bel or Sourcieux. The northern part furnishes a more compact ore than that from Chessy. Most of it is non-cupreous, but there is also a vein with 4 or 5 per cent. copper; the gangue is mostly sulphate of baryta. Much more important is the southern part of this bed, the "masse de Bibost." The ore is here very rich in sulphur, green with yellow reflection, and very friable, so that there is almost as much smalls as lumps; the gangue is almost entirely siliceous. The beds in the South of France are more numerous, but much less important. The most considerable mine is that of Saint-Julien-de-Valgalgues, in the Départment du Gard; there is another mine at Soyons, in the Ardèche. The other French mines are of little importance. A detailed description of the French pyrites-mines has been given by Girard and Morin (*Comptes rend.*, 1875, lxxxi. p. 199; *Ann. Chim. Phys.* [5],

	Chessy.		Saint-Bel.				Masse de Bibost.	
	Lumps.	Smalls.	Non-cupreous.	Cupreous.	55 metres underground.		50 metres underground.	115 metres underground.
					I.	Iª.		
Sulphur . . .	47·34	48·57	46·62	37·89	47·1	47·98	53·89	52·49
Iron . . .	41·72	43·20	39·07	29·92	40·5	41·11	46·46	46·43
Copper . . .	0·05	trace	.	4·61	...	...	...	...
Zinc . . .	..	..	...	6·36	...	...	...	...
Arsenic . . .	0·02	trace	0·05	0·06	trace	trace	slight trace	slight trace
Gangue . . .	10·79	4·71	13·92	21·25	12·4	10·78	0·37	0·90
Moisture . . .	0·08	3·52	0·17	0·09	...	0·20	0·04	0·04

	Saint-Julien.				Soyons.
	Outcrop (picked).	32 metres underground.	50 metres.	87 metres.	
Sulphur	49·11	44·13	42·87	41·13	43·94 to 49·68
Iron	43·24	38·24	37·94	36·85	39·15 ,, 43·04
Arsenic	0·11	0·05	0·10	0·08	0·16 ,, 0·39
Calcium carbonate	2·55	5·52	2·86	9·69	...
Magnesium carbonate . . .	trace	trace	trace	0·08	...
Calcium sulphate	..		...	...	0· ,, 1·67
Calcium fluoride	1·09	trace	trace	trace	trace ,, 0·62
Insoluble	2·48	10·20	13·19	11·23	4·15 ,, 11·76
Oxygen in excess	...	...	1·40	0·38	0· ,, 1·02
Moisture	1·33	1·74	1·59	0·57	0·85 ,, 4·58

vii. p. 229); from this paper the following analyses are extracted, which seem more trustworthy than those by Mène, given in the 1st edition of this book, p. 92, from the *Monit. Scient.*, 1867, p. 410.

These analyses may be summed up as follows:—The pyrites from the Rhone and Sain-Bel, on an average, contains 46 to 48 per cent. of sulphur and 10 to 12 per cent. of gangue, consisting of clay, sand, and barytes. In the southern part of the district of Sain-Bel the percentage of sulphur rises to 50 or 53, and the gangue is inconsiderable and free from barytes; arsenic is not present in quantities sufficient for determination. In the district of St Julien (Le Gard) pyrites is not found in the clay-slate, as at Sain-Bel, but in the Lias or Trias; the sulphur varies from 40 to 45 per cent.; the gangue is calcareous, and varies from 3 to 6 per cent.; arsenic is present up to 0·1 per cent., sometimes also fluorspar in quantities sufficient for estimation. The pyrites from Ardèche contains from 45 to 50 per cent of sulphur; the gangue is clay, free from lime; arsenic occurs up to 0·3 per cent.; fluorspar sometimes occurs in injurious quantities; the hydrofluoric acid given off from it in one case destroyed the glass apparatus for spreading the nitric acid, and the latter thus got to the chamber-bottom and corroded it.

In 1874 there were used in France 178,400 tons, of the value of £240,000. Of this the beds of Sain-Bel, which supply two-thirds of the French factories, contributed 120,000 tons, those of St Julien (in the department Gard) 24,600 tons, those of Le Soulier (Gard) 6000 tons, those of Soyons (Ardèche) 900 tons. Girard and Morin give twenty-three analyses of French and five of foreign pyrites used in France.

According to Scheurer-Kestner (Wurst, *Dict. de Chimie*, ii. p. 138) the pyrites from Chessy and Sain-Bel contains 45 to 48 per cent. of sulphur with very little arsenic and selenium, that from Chessy also 1 or 2 per cent. of copper and zinc. The copper is obtained from the cinders, at least at the Chessy works, by allowing them to lie for a time and moistening them: the liquid running off contains copper and zinc sulphates; and the copper is got from it by cementation. Nearly all French works, as well as those in Alsace and Switzerland, obtain their ore from those two pits; only the works at Gard and Marseilles get it from Alais, where the pyrites contains 38 to 42 per cent.

of sulphur; a few factories in the north of France use Belgian pyrites, those in the south use Spanish pyrites.

The production of pyrites in France was:—

1891.	243,030 tons.	1901.	307,000 tons.
1892.	226,904 „	1902.	318,000 „
1893.	227,288 „	1903.	322,000 „
1894.	278,452 „	1904.	271,000 „
1895.	248,934 „	1905.	267,000 „
1896.	295,325 „	1906.	265,000 „
1897.	298,571 „	1907.	283,000 „
1898.	306,002 „	1908.	285,000 „
1899.	313,087 „	1909.	273,000 „
1900.	305,000 „		

Italy possesses beds of pyrites in several places. Those occurring in the province of Bergamo, tested in Vienna (Wagner's *Jahresber.*, 1879, p. 272), are composed as follows:—

	Rodolta quarry.	Passevra quarry.	S. Guiseppe pit.	Vallantica pit.
Iron	36·29	41·72	48·35	36·79
Copper	trace	trace	0·07	1·69
Zinc	trace		0·18	...
Lead	...	...	...	trace
Silver	.	.	...	0·014
Sulphur	39·32	44·36	30·97	41·56
Arsenic	0·53	0·14	...	0·18
Alumina	2·37	1·28	1·86	1·25
Lime	5·89	0·88	1·70	0·37
Magnesia	0·66	0·39	0·14	0·10
Silica	7·16	9·68	10·45	16·40
CO_2, O and H_2O (by diff.)	7·78	1·55	6·28	1·646
Total	100·00	100·00	100·00	100·00

In the Val d'Aosta there are several mines, some of which contain a strongly arsenical pyrites.

Those at Brosso, near Ivrea, belonging to Messrs Sclopis & Co., yield pyrites containing very little arsenic: present output about 20,000 tons per annum. One quality contains 48 or 49 per cent. of sulphur and 0·2 of arsenic, the other nearly 50 of sulphur and only traces of arsenic. It is too explosive for burning in lumps, but excellent for burning as smalls. Another mine is at Pré St Didier in the same valley. This Aosta pyrites mostly requires special contrivances for getting rid of the arsenic in burning; the cinders are worked for copper, silver, and gold.

Pyrites in quantity is also found at Agordo (Cadore), Sestri Levante, and of very good quality in Sicily. The whole of the 24 Italian sulphuric-acid works burn pyrites, partly imported from Spain (Candiani, *Chem. Ind.*, 1895, p. 153); none of them burn brimstone.

The production of pyrites in Italy was:—

1897	57,383 tons
1898	66,120 „
1899	75,308 „

In 1910, Italy produced 135,628 tons ordinary and 30,060 tons cupriferous pyrites.

Swedish pyrites, from Fahlun, varies between 43 and 48 per cent. of sulphur. This ore is obtained as a by-product in the getting of copper-ores, and is said to exist in enormous quantity; but, owing to the difficulty of transit, its exportation does not pay. It is said to burn well.

Analyses of Swedish Pyrites.

	Pattinson.		Browell and Marreco
Sulphur	43·70		38·05
Iron	39·01		42·80
Copper	0·60		1·50
Lead	0·12		...
Zinc	2·57		...
Lime	0·85		...
Magnesia	0·69		...
Arsenic	trace		...
Insoluble	11·66		12·16
Oxygen, as Fe_2O_3	0·22	Oxygen and loss	5·49
Water	0·20		...
	99·62		100·00

The exportation of pyrites from Sweden in the year 1909 was 16,104 tons.

In *Norway* there exist very large beds of pyrites, many of them containing copper. Of the many pits formerly worked there, all those had to stop which produced ores with only from 35 to 40 per cent. of sulphur. The richer ores, even those free from copper, have maintained their position to some extent, because they burn well, are easily lighted, keep the heat well, do not "scar," etc. They are mostly hard and difficult to break. The most considerable pits are those of Ytteröen, which export *viâ* Drontheim; they supply 6000 to 8000 tons per annum. A large mass of cupreous pyrites, with 45 per cent. of sulphur and 3 of copper, at Vigsnaes, was worked by an Antwerp Company, but is now exhausted. Norwegian pyrites contains very little arsenic. Other pits exist thirty miles from Drontheim, on the Hardanger Fjord, near Bergen, etc. The Norwegian pyrites is more in favour as a sulphur-ore (excepting its difficult breakage) than as a copper-ore; its cinders do not very well suit the copper-works.

Analyses of Norwegian Pyrites.

	Pattinson.		MacCulloch	
	Ytteroen ore.	Drontheim ore	I	II.
Sulphur . . .	44·50	50·60	46·15	38·17
Iron . . .	39·22	44·62	44·20	32·80
Copper . . .	1·80	trace	1·20	1·10
Zinc . . .	1·18	1·34	2·10	2·32
Lead		trace	..	
Lime	2·10	trace	.	..
Calcium Carbonate .	.	. .	2·55	11·90
Magnesia . . .	0·01	trace	..	...
Magnesium Carbonate	...		...	1·08
Carbonic acid . .	1·65	. .	...	...
Arsenic . .		...	...	trace
Insoluble . . .	9·08	3·15	3·20	12·20
Oxygen, as Fe_2O_3	0·45		.	...
Moisture . . .	0·17	0·20	0·40	0·25
Total . .	100·16	99·91	99·80	99·82

The following information is due to Mr Knudsen, manager of the Sulitjelma mine (through Dr Hasenclever). Norway exported in 1901 about 90,000 tons pyrites from the following pits:—

Sulitjelma, near Bodoe .	35 to 36,000 tons	with	45 p.c. sulphur
Killingdal	25,000	„	43 to 44 p.c. sulphur
Roros, near Trondhjem .	15,000	„	43 „ 44 „
Bossmo „ .	15,000	„	48 „ 50 „

By far the largest mine is the first-mentioned, which is expected to yield an additional 20,000 or 25,000 tons in 1902 and is reckoned to last for centuries to come. It contains very little arsenic. Much ore, richer in copper and poorer in sulphur, is also smelted on the spot. The ore from Killingdal and Röros is also cupreous; and that from Bossma is free from copper, with traces of arsenic. The following mines are not yet worked, for want of railway communication:—Foldal, Vaarteigen, and Nudal. They test 43 or 44 per cent. S, and at most 2·5 per cent. Cu, and might yield from 60,000 to 90,000 tons per annum.

Detailed communications on the exportation of pyrites (and iron ores) from Norway and Sweden have been made by J. H. L. Vogt (*Z. Elektrochem.*, 1903, p. 856; and *Verhandl. d. V. intern. Kongr. f. angew. Chem.*, 1904, ii., pp. 90 *et seq.*). The same estimates the production of pyrites in Norway for 1906 = 900,000 tons [?] (*Chem. Zeit.*, 1907, p. 269). In 1909 the exportation of pyrites from Norway yielded nearly 5,000,000 Kroner. In 1910 the production was 320,000 tons, and for 1911 it is estimated at 400,000 tons (*Chem. Ind.*, 1911, p. 755)

In *Russia* a good many beds of pyrites exist, some of which are utilised for the manufacture of sulphuric acid, especially those in the Ural. The Russian pyrites beds are enumerated in *Chem. Trade J.*, 1911, xlix. p. 29, and l., p. 71; and in *Eng. and Min. World*, 14th October 1911. Pyrites is found in Central and South Russia, and in the Caucasus, but most of it in the Ural districts, far from the centres of chemical industry. It contains about 30 per cent. S and much carbon, which makes it unsuitable for the production of sulphuric acid by the contact process. The Ural pyrites splits in roasting and gives off much dust. In 1908 the production in the Ural was 50,000 tons, in Central Russia 2500 tons, in the Caucasus about 5000 tons: total 57,500 tons. The importation of foreign pyrites in 1908 was 90,000 tons; in 1910, 110,000 tons.

Spain and Portugal possess the largest known beds of pyrites. Much of it is cupriferous, and all of it is distinguished by its very good behaviour in burners; so that the burners have been built very much lower for it, and much labour is saved. This pyrites has only been worked again since 1855; but the Romans, and before them the Phœnicians and Carthaginians, knew it very well, as is shown by many traces. The bed, however, was at that time only worked where it was richest in copper. According to Schönichen (*Dingl. polyt. J.*, clxx. p. 448) all the beds are within a belt of 5 leagues width, reaching, parallel to the Sierra Morena, from the western frontier of the province of Seville, across the hilly country situated to the south of this, right through Portugal to the Atlantic Ocean—a distance of 30 leagues. The prevailing rocks in that country are clay-slate and crystalline slates; but parallel to the granitic tract of the Sierra Morena felsite-porphyry and quartzite have broken through the slate, and only in the neighbourhood of such dykes are the pyrites-beds found. Their shape is that of large lenticular pockets in the metamorphic clay-slate, from 20 to 36 fathoms thick, and extending to a length of 170 to 260 fathoms. The whole bed is filled with pure pyrites, without any visible gangue. The ore is in a few places found at only 1 or 2 fathoms below the surface, undecomposed, and in a sandy state, so that it can be got by daylight work. In other places the zone of decomposition reaches from 10 to 50 fathoms downwards. The percentage of copper varies from 2½ to 40; but ores with more than 10 per cent. of copper are only contained in small vertical zones within the large masses. Only these "black" ores were the object of the mining-operations on the part of the Phœnicians and Romans. The quantity of pyrites existing there is almost inexhaustible, and can certainly supply the requirements of mankind, both of copper and of sulphur, for thousands of years to come.

Special highways, and latterly also railways, have been made in order to facilitate the communication with the ports of Huelva, San Lucar du Guadiana, and Pomaron; but a great deal of the ore is still conveyed for some distance on mule-back.

Of the various companies which had been formed for working this ore most have ceased to exist; and only four or five remain, all of them in English and French hands. The smallest of these is the Buitron Pyrites Company, which works the mines of Buitron and Poderosa. The Tharsis Sulphur and Copper Company possesses much more extensive mines, a railway of its own, a wharf at Huelva, and also a number of works in England and Scotland for the wet extraction of the copper from the cinders returned to them. The Tharsis ore is very good, but very soft, and makes much dust in breaking. The San Domingo mine lies in Portuguese territory; its ore is known as Mason's ore, and is considered superior to all others, so that it commands a better price. The last, but largest, of these companies is the Rio Tinto Company, which has thrown such large quantities of pyrites into the English market that, from 1875 to 1876, prices receded by more than one-third. Its ore is also of excellent quality. The mines of Carpio and Lagunazo, in the province of Huelva, are not yet worked for exportation.

The Spanish (and Portuguese) pyrites never contains less than 46, and up to 50 per cent. of sulphur, besides 3 to 4½ per cent. of copper, which, however, by most of the English buyers, is not bought, but returned in kind to the seller in the shape of cinders from the pyrites-burners. The value of the copper (if bought) is still fixed by the so-called "Cornish assay"—that is, a process of dry assaying known only to a few assayers living at Redruth and other places in Cornwall, the great inaccuracy of which is perfectly well known to all parties concerned: it shows, for instance, only 2 per cent. if 4 per cent. is actually present; and from this difference the buyer must pay the cost of extracting the copper and his own profit, since the price to be paid for the copper *in the ore* by Cornish assay is sometimes higher than the value of a similar quantity of copper *metal*. This remarkably irrational system has not hitherto been done away with for sales.

In Germany also in 1877 a number of manufacturers united in working Spanish pyrites (especially Rio Tinto ore), and in delivering all their cinders to the Duisburg copper-works. The Oker works also use similar ores, which they work up themselves for copper.

The ore of the three principal companies is very similar in composition; its analysis is as follows:—

	Pattinson.				Claudet (San Domingo ore).	MacCulloch (San Domingo ore).
Sulphur . . .	48·00	49·60	44·60	49·30	49·00	49·80
Iron . . .	40·74	42·88	38·70	41·41	43·55	42·88
Copper . . .	3·42	2·26	3·80	5·81	3·20	2·26
Lead . . .	0·82	0·52	0·58	0·66	0·93	...
Zinc . . .	trace	0·10	0·30	trace	0·35	0·10
Lime . . .	0·21	0·18	0·14	0·14	0·10	0·18
Magnesia . .	0·08	trace	trace	trace	...	...
Thallium . .	trace	trace	trace	trace	...	...
Arsenic . .	0·21	0·28	0·26	0·31	0·47	0·28
Insoluble . .	5·67	2·94	11·10	2·00	0·63	2·94
Oxygen, as Fe_2O_3	0·09	0·15	0·23	0·25	1·07	...
Moisture . .	0·91	0·95	0·17	0·05	0·70	0·95
Total . .	100·15	99·86	99·88	99·93	100·00	99·39

The following analyses represent the average quality:—

	Rio Tinto.			S. Domingo.		Tharsis Bartlett.
	Cumenge.	Caron.	Rivista Min. 23	Pattinson	Bartlett.	
Sulphur . .	48·09	50·7	49·00	49·90	49·80	47·50
Iron . .	40·00	41·3	43·55	41·41	43·55	41·92
Copper . .	3·42	3·5	3·20	2·46	3·20	4·21
Lead . .	0·82	..	0·93	0·98	0·93	1·52
Zinc . .	trace	...	0·35	0·44	0·35	0·22
Arsenic . .	0·21	...	0·47	0·55	0·47	0·38

A new pyrites-mine has been opened in Spain, called St Mardy Tinto Santarossa. Its product has been found by Lunge and Banziger (*Z. angew. Chem.*, 1896, p. 421) to contain 0·85 per cent. moisture, 5·20 insoluble, 43·87 sulphur, 42·12 iron, 1·09 arsenic, 2·15 antimony, 3·17 copper.

Some kinds of Spanish pyrites are in bad repute with the manufacturers as "explosive," or "detonating," because they decrepitate in the kilns shortly after lighting with loud detonations, and thereby make so much fine powder that the burners are stopped up and "scars" are formed. The reason of this detonating property is probably to be sought in the presence of hydrated silicates (zeolites) in the ore. Best and the United Alkali Co. (B. P. 7915 of 1905) subject such pyrites to a preliminary heating by means of an apparatus, shown in the specification, before charging it in the pyrites-burners. The explosive pyrites from Goshen Copper Mine, near Scull Harbour, County Cork, is said to contain confined carbon dioxide and water (Blount, *J. Soc. Chem. Ind.*, 1885, p. 674).

Recently hundreds of thousands of tons of "leached ores" have come into the market from Spain, especially Rio Tinto and Pomaron. These ores are exposed to the weather and then washed with water, in order to extract the copper, of which they retain only 0·3 to 0·5 per cent. They test 49 or 50 per cent. sulphur in the dry state, but they generally contain about 5 per cent. water. In the pyrites-burners they make very much dust, as they are very porous and friable.

According to Hjelt the average percentage of arsenic in Spanish ores is 0·91.

Pyrites with very little or no copper is also found in Spain.

One of the best descriptions is that of the Aguas Teñidas mine, containing iron 46·60 per cent., sulphur 53·15 per cent., silica 0·20 per cent., arsenic, copper, selenium, silver and gold traces. It is sold both in the state of lumps and smalls. It burns very easily down to 1·0 or 0·5 per cent. of sulphur, so that the cinders, which contain 68·5 per cent. of metallic iron, and no copper, phosphorus, lead, or zinc, are very valuable for blast-furnaces. The annual sales have exceeded 200,000 tons, but for some time very little has come into the market owing to an accident at the mine.

H. J. Davis of New York, one of the principal importers of pyrites to the United States, gives the following analyses of very good, hard Spanish ores containing but little copper:—

	Aracena	Balmacea	San Tolmo.
S	51·77	50·19	46·40
Fe . . .	45·53	4[illegible]·61	40·11
Cu . . .	0·29	0·20	[illegible]·90
Si . . .	1·90	3·00	11·27
As . . .	?	?	none

The production of iron-pyrites (non-cupreous) in Spain, according to *United States Mineral Resources*, for 1900, p. 826, was as follows:—

1891. 279,161 tons.
1892. 435,906 „
1893. 393,453 „
1894. 511,769 „
1895. 480,255 „
1896. 98,393 tons (?)
1897. 217,545 „
1898. 255,896 „
1899. 316,212 „

The production of cupreous pyrites and its exportation by the three principal firms in Spain and Portugal was, according to the same authority, p. 186:—

1. Rio Tinto Co.

1898. Production 1,465,380 tons (2,852 per cent. Cu).
1899. „ 1,649,844 „ (2,719 „ „).
1900. „ 1,894,504 „ (2,744 „ „).
Exportation in 1900: 704,803 tons.

2. Tharsis Sulphur & Copper Co.

1899. Production 572,854; exportation 222,475 tons.
1900 „ 468,738; „ 220,019 „

3. Mason & Barry, Ltd. Exported:

1899.	339,298 tons.
1900.	394,740 „

Enormous quantities of cupreous pyrites are roasted and worked for copper in Spain, without utilising the sulphur, as is apparent from the above figures.

In the year 1909 Spain exported 1,360,325 tons and Portugal 74,419 tons pyrites of all sorts.

In the *Z. angew. Chem.*, 1905, p. 759, the following statements are made on Spanish pyrites. New facilities for shipping ore have been provided at Huelva and at some new railway stations. At Huelva in 1904 about two million tons of pyrites have been shipped. The Tharsis Co., the Rio Tinto Co., and the Buitron Co. have opened out new mines. The Rio Tinto Co. was erecting superphosphate works to utilise the excess of their ore.

According to Reusch (*Chem. Zeit.*, 1906, p. 326) the Rio Tinto Co. has discovered new beds of pyrites which allow it to maintain the present production for another hundred years; so has also the Tharsis Co., which will be able to supply several millions of tons of pyrites in excess of what it had counted upon four years previously.

The *United States of North America* are very rich in pyrites. The principal mines worked at present are the following:—

In New Hampshire: the Milan mines, Coos County. The ore is of excellent quality, and is now sorted into two grades, of the following composition:—

	No. 1.	No. 2.
Sulphur	46·0	35·0
Copper	3·7	5·0
Iron	40·0	30·5
Silica	6·2	25·5
Zinc	4·0	8·0
Arsenic	0	0

No. 1 is in special favour, but No. 2 burns very well and is readily bought. Smelting-works exist for extracting the copper and silver.

New York: 2000 tons were raised at Hermon, County St

Lawrence; sulphur contents, 38·0 per cent. Another mine in Ulster County, with 39 per cent. ore, was worked till stepped by an inrush of water.

Virginia: Arminius Copper Mines Co. and Sulphur Mines Co., both in Louisa County. The ore contains 49·5 per cent. sulphur, 0·5 copper, 43·5 iron, 6·4 silica, etc. Other mines are in Prince William and Palaski counties. Virginia was the larger producer of pyrites in the United States in 1909.

Alabama: near Pyriton, Clay County.

California produced more pyrites in 1909 than any other state except Virginia, near Oakland, Alameda County, and near Keswick, Shasta County.

Georgia: near Acworth, Cherokee County, and Villa Rica near Atalanta. The production in 1909 was less than in 1908.

Illinois: the production in 1909 greatly exceeded that of 1908. The pyrites is obtained chiefly as a by-product in the mining of coal.

Indiana: the same remark to be made as in the preceding case.

Massachusetts in 1909 produced less than in 1908. The principal old mine, at Charlemont in Davis County, caved in during the year, but a new shaft was sunk. Another mine, at Mount Peak, was not working in 1911.

Ohio: the production of pyrites from coal increased in quantity and value.

Pennsylvania produced a little pyrites in 1909 in Mercer County. So did Wisconsin.

Ektel (*U.S. Geol. Survey Bull.*, No. 213, p. 62) describes a new occurrence of pyrites, the Chestatee lode, in Lumpkin County, Gainsville, Ga., 30 ft. thick, and proved for 250 ft. Composition: 43·52 per cent. S, 39·70 Fe, 3·09 Cu, 0·72 Zn, 2·53 Al, 0·43 MgO, *no* As, 9·26 sand, etc., 0·36 moisture.

The absence of arsenic in most American pyrites (as far as it is now worked) is a remarkable feature.

K. F. Stahl (*Z. angew. Chem.*, 1893, p. 54) quotes analyses of American pyrites. No. 1 is from Tallapoosa Mine, Georgia, 1882; No. 2 from Rogers Mine, Paulding County, Dallas, Ga.; No. 3 from Sulphur Mines Co. of Virginia, Louisa County, 1884; No. 4, Peru Zinc Co., La Salle, Ill.; No. 5 from Dodgeville, Wis.; No. 6, from the same mine as No. 3, 1891; No. 7, Davis Sulphur Ore Co., Franklin County, Mass., 1891.

	1	2.	3.	4.	5.	6.	7.
Water . .		...	2·9	..	.	1·3	0·8
Sulphur . .	45·1	37·6	39·1	50·2	43·7	40·6	42·4
Iron . . .	..	40·6	41·5	.	...	37·3	35·4
Copper . .	3·1	5·2	0·6	..	...	1·0	1·4
Zinc . . .	3·0	4·5	0·8	...	...	1·9	5·5
Cadmium . .	0·1	0·01	?		...	?	?
Insoluble . .	2·9	9·5	14·7		1·4	10·5	5·1
Arsenic . .	?	?	0·02	.	..	trace	trace

We quote from the volumes of *Mineral Industry* and the *U.S. Geological Survey* the production, imports, and consumption of pyrites (not containing more than 3·5 per cent. Cu) in the United States, not counting the auriferous pyrites used for the manufacture of sulphuric acid in Canada, expressed in long tons of 2240 lbs.:—

Year	Production.	Importation.	Consumption.
1891	100,319	130,000	239,319
1892	106,250	210,000	316,250
1893	95,000	194,000	289,000
1894	107,462	146,023	253,485
1895	81,000	190,436	271,436
1896	109,282	199,678	308,960
1897	133,368	259,546	392,914
1898	191,160	171,879	363,039
1899	178,408	310,008	488,416
1900	201,317	329,449	530,766
1901	254,825	403,706	638,531
1902	207,874	440,363	...
1903	233,137	420,410	...
1904	252,000	422,720	190,224*
1905	253,000	511,946	230,376*
1906	261,422	598,078	269,135*
1907	247,387	627,985	282,593*
1908	222,598	668,118	300,653*
1909	210,000	688,843	...
1910	238,154	803,551	...

* The figures for the pyrites consumed since 1904 denote, not the weight of the pyrites itself, but that of the sulphur contained therein.

We may take it that, roughly speaking, about half of the sulphuric acid produced in the United States is made from brimstone, and half from pyrites. Most of the American pyrites, including the Newfoundland ore, is granular and more fit for fines' burners than for lump burners.

In *Canada* there are two mines: the Albert mine and the Crown mine. They supplied the first pyrites used in the United States for making oil of vitriol. Sulphur 40·0 per cent., iron 35·0, copper 4·0, silica 20·0. Output:

1891.	60,474 tons.	1896.	30,103 tons.
1892.	53,372 „	1897.	34,471 „
1893.	52,270 „	1898.	24,721 „
1894.	36,185 „	1899.	35,742 „
1895.	30,534 „		

The exportation of pyrites from Canada in 1909 was 57,038 tons.

In *Newfoundland*, on Piney's Island, there is a very large bed of pyrites, accessible by a shaft 60 ft. deep. The bed is 72 ft. wide, and 28 ft. of it contains 3 or 4 per cent. copper. This ore is very easy to roast; an analysis of the non-cupreous ore showed Cu 0·07, S 51·16, Fe 48·35, SiO_2 0·13, CaO 0·22, As 0·02; no Sb, Pb, Zn, Bi (*Eng. and Min. J.*, 1892, p. 467).

In *South Australia* pyrites is found with 48·7 per cent. S and 2·8 per cent. Cu (Mène, *Monit. Scient.*, 1867, p. 411).

In *North Borneo* pyrites has been found, containing 45·48 per cent. S, 37·38 per cent. Fe, 5·62 per cent. Cu, 7 gr. Au, and 1 oz. 22 gr. Ag per cwt. (*Chem. Zeit.*, 1909, p 82).

The *World's production* of iron-pyrites (in tons) is stated in the various volumes of *Mineral Resources of the United States*, from official sources. (I cannot explain the difference between these and the other "official" figures given in various places *suprà*.) See Tables, pp. 86-88.

According to Quincke (*Z. angew. Chem.*, 1909, p. 2029) the *consumption of pyrites* in that year was about one million tons in Germany, 800,000 tons in Great Britain, 800,000 tons in the United States, and 700,000 tons in France.

The *price* of pyrites in the English trade is always so much for each per cent of sulphur per ton, called a "unit," and has come down from nearly 1s. per unit, in the years from 1860 to 1870, to something like 3d. since about 1885, and 4d. to 4½d. in 1911. For copper above a certain minimum percentage a special allowance is made. The burnt ore (cinders), if non-cupreous, are given back to the seller, or remain the property of

	1895.	1896.	1897.	1898.	1899.	1900.	1901.
Belgium*	3,510	2,560	1,828	147	283	410	...
Bosnia & Herzegovina	.	2,000	3,670	240	430	1,700	4,570
Canada	31,024	30,586	35,299	29,228	25,117	56,316	...
France	253,416	282,064	303,448	310,972	318,832	305,073	302,605
Germany	127,036	129,168	133,302	136,849	144,623	169,447	164,954
Hungary-Austria . .	69,195	52,697	44,454	58,079	79,519	8,000	92,428
Italy	38,586	45,728	58,320	67,191	76,538	71,616	87,969
Newfoundland . .	34,879	27,712	33,316	33,100	31,500	33,000	. .
Norway	61,994	63,507	94,484	89,763	90,000	95,000	105,000
Portugal* . . .	200,000	200,000	210,265	248,218	275,658	345,330	331,641
Russia	11,042	11,550	19,380	20,000	25,000	25,000	?
Spain†	60,267	100,000	217,545	260,016	319,285	356,018	393,397
Sweden	221	1,009	517	386	150	179	
Great Britain . .	9,193	10,178	10,753	12,302	12,426	12,484	10,241
United States . .	107,371	117,782	128,468	194,219	181,263	204,538	...
Total . . .	1,007,734	1,073,541	1,295,049	1,460,710	1,580,624	1,743,111	...

* For Portugal the output for 1895 and 1896 is roughly estimated. For this country only pyrites with less than 1 per cent. copper is included. For 1908 only cupreous iron pyrites is given.

† For Spain the cupreous pyrites, from which copper is extracted, is not included. *Cf.* p. 79.

	1902.	1903	1904.	1905.	1906	1907	1908.	1909.
Belgium	...	709	1,058	961	894	390	351	211
Bosnia & Herzegovina	..	6.484	10.257	18,765	13,262	7,969	10.238	?
Canada	...	33,039	29.400	29,236	35.365	41,288	42,264	57,718
France	...	324,212	267,268	262,907	261,084	278,543	280.233	268,918
Germany	...	168,307	172,030	132.448	163.869	192.913	216,000	195,960
Hungary-Austria	...	95,560	95.618	105,165	110,849	109.682	97,268	97,412
Italy	...	99,857	110,240	115.814	120 437	125,000	129,647	130,152
Newfoundland	...	42,000	60.200	50,720	28,132	22,310	?	?
Norway	...	127,887	131,497	159,461	194.770	232,381	264,891	278.352
Portugal*	...	370,253	377 540	346.928	345.222	359.616	80,135†	194,861
Russia	...	...	...	..	30 019	?	?	?
Spain†	...	153,543	159,292	176,258	186,262	186.023	259,308	254,853
Sweden	..	7,670	15,705	20,435	21,483	20,583	29,103	15,850
Great Britain	..	9,639	10,287	18,745	13,262	7,969	9,448	8,429
United States	...	233.137	207.081	253,000	261 422	247.387	222,598	247,070
Total	.	1,691,717	1,693,192	1.742,686	1,814,410	?	?	?

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* For Portugal the output for 1895 and 1896 is roughly estimated. For this country only pyrites with less than 1 per cent. copper is included. For 1908 only cupreous iron pyrites is given.

† For Spain the cupreous pyrites, from which copper is extracted, is not included.

Average Composition of the World's Pyrites.

(From *United States Mineral Resources*, 1886, p. 652.)

Localities.	Sulphur.	Iron.	Copper.	Arsenic.	Zinc.	Lead.	Carbonate and Sulphate of Ca and Mg.	Silica.
Milan mine, New Hampshire, No. 1	46·00	40·00	3·75	trace	4·00	none	...	6·25
,, ,, No. 2	35·00	30·50	5·00	none	8·00	...	...	21·50
Davis mine, Mass . . .	49·27	45·30	1·47	trace	...	...	...	3·83
Elizabeth mine, Vermont . .	32·00	50·00	3·50		...	...	...	13·50
St Lawrence Company, New York	38·00	34·00	3·00		...	...	...	25·00
Arminius mine, Va. . . .	46·00	44·50	2·10		...	...	...	7·40
Capelton, Canada . . .	40·21	35·20	5·10	trace	...	...	8·00	12·00
Rio Tinto, Spain	48·50	40·92	4·21	0·33	0·22	1·52	0·90	3·46
Tharsis, Spain	49·90	42·55	3·10	0·47	0·35	0·93	0·87	2·20
S. Domingo, Portugal . . .	49·07	44·28	3·25	0·38	...	...	0·93	2·59
Swedish mines Average	38·05	42·80	1·50	none	...	...	5·09	12·56
Norwegian ,, . . ,,	46·15	44·20	2·10	trace	1·20	...	2·50	3·65
French ,, . . ,,	46·60	39·70	none		...	...	0·20	13·50
German ,, . . ,,	45·60	38·52		0·95	6·00	0·74	...	8·19
Belgian ,, . . ,,	42·80	36·70		0·20	0·40	0·92	5·45	12·47
English ,, . . ,,	34·34	32·20	0·80	0·91	1·32	0·40	...	30·03
Irish (?) ,, . . ,,	47·41	41·78	1·93	2·11	2·00	...	...	4·77

the buyer, as may be agreed. Cupreous cinders are either sent to a copper work, or the copper is extracted by the buyer, and the ferric oxide remaining sold to iron works.

Carriage of Pyrites.

Pyrites, whether lumps or smalls, is always carried in bulk, both by sea and in railway cars. Mastbaum (*Chem. Zeit.*, 1912, p. 30; *Chem. Trade J.*, l. p. 358) reports a case where a steamer was damaged by its cargo of pyrites, which must have contained too much water, getting into a pasty state, and shifting about with the movements of the steamer. In several places a strong acid liquid had collected.

Proportional Value of Poor and Rich Pyrites.

It is no matter of surprise that the rich and at the same time well-burning Spanish ores, and those ores similar to them elsewhere, where they could be imported, have driven the poor ores out of the field. An ore of 35 per cent., like that from Wicklow, even for the same weight of sulphur, has much less value than a 45-per-cent. ore. The wages for breaking and burning the ore in both cases must be ruled by the gross weight of the ore, and consequently for equal weights of sulphur come to much more with poor than with rich pyrites; moreover, under conditions otherwise equal, the unburnt sulphur in the cinders is the same by weight. If, for instance, 5 per cent. of sulphur are left in the cinders, this amounts with 35-per-cent. ore to $\frac{5}{35} = \frac{1}{7}$; with 45-per-cent. ore to only $\frac{5}{45} = \frac{1}{9}$; the proportion to be kept in view is accordingly not $35 : 45 = 7 : 9$, but $30 : 40 = 3 : 4$. Furthermore, the same holds good of cost of plant and repairs and of wages, and, lastly, since the poor ores generally contain no copper, also of the cost of removing the cinders.

Therefore, unless the burning is nothing but a preparation for the metallurgical treatment, where the sulphur is quite of secondary importance, the ores poor in sulphur are always avoided as much as possible.

Analysis of Pyrites.

In the analysis of pyrites for technical purposes, in the first instance the percentage of sulphur is taken into account; and it is therefore mostly the custom to estimate only this and, perhaps, also the moisture. If the ore has afterwards to yield copper, this must of course also be considered; but where the copper, as is mostly the case, is not bought by the vitriol-maker, but the cinders are returned to the seller, the estimation of copper is generally omitted in the chemical works as unnecessary. This restriction to the estimation of sulphur ought, however, only to take place with pyrites from well-known localities, whose general composition and properties are well known, and where the salient point is only the percentage of the most important constituent, viz. the sulphur. Each cargo, even each portion of a cargo going to a separate buyer, is sampled in the presence of both the buyer's and seller's agents, according to well-understood rules; the sample is broken up, reduced, and sealed up in bottles, which are sent to an analytical chemist (generally mentioned in the contract note); this chemist's certificate rules the price to be paid for the pyrites down to ¼ per cent. If, for instance, a sale has been made at 6d. per "unit," this means that for each per cent. of sulphur found the sum of 6d. per ton is paid; thus for 48¼ per cent. of sulphur 48¼ × 6d. = 24s. 1½d. per ton. The ton is generally calculated = 21 cwt.; that is to say, the buyer receives an allowance in weight of 5 per cent.

The first treatment of the pyrites in analyses, in the majority of cases, is by the *wet* way, by fuming nitric acid or aqua regia; but the prescriptions differ in details. The decomposition was formerly frequently made, according to Fresenius's prescription, by means of red fuming nitric acid, which it is sometimes difficult to obtain free from sulphuric acid, and which is unpleasant to handle. In lieu of this, sometimes chlorate of potash together with hydrochloric acid, or, still better, with nitric acid of 1·36 sp. gr. have been used. I have always found the best, safest, and cheapest way to employ aqua regia, made from 1 part of fuming hydrochloric acid and 3 or 4 parts of nitric acid of 1·36 to 1·4 sp. gr., and this mixture is now used in most places. The mineral is converted into an impalpable powder and passed through the finest silk gauze; the triturating ought to be done first in a steel mortar or by wrapping it up in paper and smashing with a hammer, and then in an agate mortar, *not* in a porcelain or Wedgwood mortar. The powder is treated with about 50 parts of aqua regia; if no reaction takes place at once, it should be gently heated on a water-bath till the reaction sets in; but then the beaker should be removed instantly from the water-bath, and only replaced when the reaction slackens; thus the decomposition is generally complete in ten minutes. The operation should be performed in a large beaker, or, still better, in an Erlenmeyer flask covered by a funnel or a watch-glass, lest any loss should take place by spurting; and the work must be done under a draught-hood, on account of the mass of acid vapours given off. If the decomposition should not be perfect after heating some time, some more aqua regia is added and the heating continued; but mostly this will be caused by the powder not being sufficiently fine, and the analysis in this case cannot easily be finished. In this way of decomposing the ore, which is both quick and safe, the disagreeable separation of sulphur happens very rarely. If it does, the sulphur is oxidised by cautiously adding a little chlorate of potash.

The residue from the solution will contain silica and silicates, perhaps a little lead or barium, both as sulphates. Although their sulphur is thus not estimated, no harm is done, as it is anyhow valueless to the manufacturer. Lead sulphate is pretty soluble in concentrated acids, but it is almost entirely precipitated again by the immediately following treatment.

At all events the whole of the nitric acid present must be destroyed or removed, because the estimation of sulphuric acid by barium chloride in the presence of nitric acid or its salts gives results much in excess of the truth. The whole is therefore evaporated to dryness on the water-bath[1] with an excess of hydrochloric acid, by which at the same time all silicic acid dissolved is made insoluble. The mass is again moistened with strong hydrochloric acid; and if on gently heating no yellow vapour and no smell of nitrous products are perceived, it is diluted with hot water and the solution filtered from the residue. Care must be taken not to employ too much hydrochloric acid, as barium sulphate is not quite insoluble in hot concentrated acids; on the other hand, enough acid must be present to dissolve all salts of iron, which cannot be doubtful if the colour and behaviour of the residue are observed.

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[1] The last evaporation may be hastened by employing a sand-bath or asbestos cardboard, taking care to remove the vessel at the moment when the mass has become dry.

Some chemists prefer to the aqua regia above described a solution of bromine in hydrochloric acid; but I have not found this to answer very well. Drown (*Chem. News*, xliii. p. 89) heats the pyrites with a solution of caustic soda or sp. gr. 1·25, adds cautiously bromine in excess, acidulates with hydrochloric acid, and evaporates to dryness.

Noaillon (*Z. angew. Chem.*, 1897, p. 351) employs a mixture of sodium chlorate and nitric acid for decomposing the pyrites, in order to avoid loss of sulphuric acid when drying the resulting mass. (Such a loss never occurs when working according to my prescription.)

Where the utmost accuracy is not desired the solution may now be at once treated with barium chloride, as follows:—

The clear solution is brought to *full boiling;* and to it during boiling a *hot* solution of barium chloride is slowly added. Lest too great an excess of this be used, it is preferable to use a measured quantity of a concentrated solution of known strength, but more than sufficient for precipitating all the sulphuric acid present. It is best to pour the hot solution of barium chloride rather slowly into the boiling solution of sulphate, with constant stirring, but it is quite unnecessary to do this drop by drop as prescribed by Gladding (*Chem. News*, lxxx p. 181); *cf.* Lunge, *Z. angew. Chem.*, 1895, p. 69, and *J. Amer. Chem. Soc.*, March 1895. If the process is carried out as described here, the barium sulphate settles down completely in a few seconds, leaving a perfectly clear liquid, and nothing of the precipitate passes through the filter. It is quite unnecessary to allow a long time for the settling. If the operation is carried on as described, the filtrate never becomes cloudy afterwards; on the other hand, the work is greatly expedited by filtering the liquid in the boiling-hot state, say fifteen or twenty minutes after precipitation. A Bunsen's filter-pump acts rather too strongly in this case; but it is very useful to employ a simple contrivance indicated many years ago by Piccard which does excellent service in other analytical operations, viz., a glass tube attached to the funnel by means of an elastic joint, with a loop causing a continuous jet of liquid to issue at the bottom (Fig. 6). The straight part below the loop may be 8 or 10 in. long; the filter must be pressed tightly to the sides of the funnel to prevent any air being sucked in. When this contrivance is used, which does not act so violently as a Bunsen pump, the liquid, so long as there is not too much precipitate in the filter, runs through in a continuous jet.

At first only the clear liquid is poured off as completely as possible from the dense granular precipitate; this is covered with *boiling* water, acidulated with a few drops of hydrochloric acid; the liquid is boiled for a few moments, and can be decanted in about two minutes' time. This operation is again repeated twice or three times, but without adding any more hydrochloric acid; the precipitate is washed on to the filter, and after very little washing the filtrate will be found perfectly neutral and free from dissolved matters. The filter is dried, the precipitate taken out, and the filter burnt, preferably in a platinum crucible laid on its side; then the precipitate is put in and ignited, not too strongly: and for each 100 parts of barium sulphate found 13·73 parts of sulphur are calculated. The ignited barium sulphate must not cake together; on moistening, it should not give an alkaline reaction; and on heating with dilute hydrochloric acid and filtering, no barium salt ought to be found in the solution.

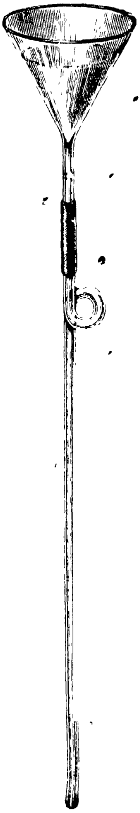

FIG. 6.

It generally happens, even if the solution before precipitation was rather strongly acid, that the precipitate is stained yellowish by precipitated ferric oxide or basic ferric sulphate, which cannot be removed even by boiling with dilute hydrochloric acid.

Although this proves the presence of a foreign substance in the barium sulphate, which ought to make the result too high, yet it is found in practice that the results are always too low. The cause of this apparent anomaly has been studied by Jannasch and Richards (*J. prakt. Chem.* [2], xxxiv. p. 321) who found that in the presence of iron a barium-ferric sulphate is precipitated, which on ignition slowly loses a portion of its sulphuric acid. If the ignition is carried on very persistently, the error thus produced may amount to a full per cent. of sulphur or upwards; but I have shown, in the paper quoted below, that with the ordinary mode of ignition it does not exceed 0·18 per cent.; hence the above-described method is always available where perfect accuracy is not required, and a speedy completion of the test is a consideration. Westmoreland (*J. Soc. Chem. Ind.*, 1887, p. 84) even contends that its results entirely agree with those obtained by my new method (an opinion to which I must demur).

Where, however, the greatest possible accuracy and freedom from error is required (and this is the case when testing an average sample of pyrites representing a whole cargo, or a large portion of such), it is necessary to remove the disturbing influence of the iron. This can be done in two different ways, by the *dry* and by the *wet* method. The *dry* method is that recommended by Fresenius (*Z. anal. Chem.*, xvi. p. 335). He prescribes decomposing the pyrites by fluxing it with 20 parts of a mixture of 2 parts of dry sodium carbonate entirely free from sulphate, and 1 part of potassium nitrate, passing carbonic acid into the solution for the precipitation of lead, boiling the residue with a solution of sodium carbonate and then with water, acidulating with hydrochloric acid, and repeatedly evaporating for the expulsion of nitric acid, after which the process is carried on as usual, the precipitation taking place by barium chloride. This process is much more troublesome and tedious than that to be described below, which employs the wet method. Another objection to it is that it estimates not merely the sulphur of the iron and copper sulphides, but also that of galena and of barium sulphate, which are entirely useless to the manufacturer of sulphuric acid (*cf.* my experiments on the action of nitric acid on lead sulphate, *J. Soc. Chem. Ind.*, 1887, p. 96). Moreover, the platinum crucibles are strongly acted upon, and coal-gas cannot very well be employed in the operation of decomposing the pyrites, as its sulphur would cause an error in the test. Hence it is advisable to use spirit-lamps of a special shape, calculated to yield the necessary heat. [The use of spirit-lamps can be practically avoided by placing the crucible in a round hole made in a piece of asbestos cardboard, in which case the products of the combustion of coal-gas are carried off sideways.]

Jene (*Chem. Zeit.*, 1905, p. 362) considers, especially for testing the sulphur in burnt ore, the dry method of Fresenius to be far more accurate than the wet treatment with aqua regia.

Gottlieb (*ibid.*, p. 688) states that this applies only to cinders from ores containing a notable quantity of barium sulphate. On the whole he prefers the dry method also for ordinary cinders.

Jarvinen (*Ann. Acad. Scient. Fennicae*, Series A., vol. ii. No. 4) recommends the very slow addition of barium chloride (long ago prescribed by Lunge). He also describes a form of the well-known method of titrating the sulphuric acid by benzidine (*ibid.*, No. 16).

Hayes (*American Chemist*, v. p. 271) describes a method of decomposing pyrites with alcoholic soda and lime, the advantages of which are in no way evident.

Fahlberg and Iles (*Ber.*, xi. p. 1187) recommend fluxing the sulphur-ore with caustic potash (25 g. to 0·1 g. of S) in a silver crucible for fifteen to twenty minutes, lixiviating the mass, oxidising the lower oxides of sulphur by bromine-water, and precipitating by barium chloride.

Clark (*J. Soc. Chem. Ind.*, 1885, p. 329) heats the pyrites with a mixture of sodium carbonate and magnesia to a dark red heat; the resulting mass is lixiviated with water whilst passing in carbonic acid, and the sulphuric acid estimated in the usual way. J. Pattison (*ibid.*, p. 724) shows that this method gives exactly the same result as mine (of course, only in cases where barium sulphate and galena are absent, which militates against Clark's process).

Lunge's Method.—Looking at the great desirability of retaining the decomposition of pyrites in the *wet* way, I have worked out a method for doing so without incurring the error caused by the presence of iron. This method was first described in the *Z. anal. Chem.*, 1880, p. 419, and has been very generally accepted for the assaying of pyrites between buyer and seller. Objections made to the accuracy of that process by Jannasch and Richards (*J. prakt. Chem.* [2], xxxix. p. 321) have been withdrawn by them (*ibid.*, xl. p. 326), and have been completely refuted by experiments made in my laboratory by two independent investigators (*Z. angew. Chem.*, 1889, p. 473). The process, as it will now be described, may hence be regarded as the most accurate known for the estimation of sulphur in pyrites, where it is desirable *not* to include galena and heavy-spar, and it is at the same time very easy and speedy of execution, if the following directions are accurately observed.

About 0·5 g of pyrites is heated with about 10 c.c. of a mixture of 3 vols. nitric acid (sp. gr. 1·4) and 1 vol. strong hydrochloric acid, both ascertained to be absolutely free from sulphuric acid. The operation is performed as described above, in such manner that no loss by spurting takes place. The mixture is heated up now and then, till the decomposition is complete, and is then evaporated to dryness in a water-bath. Now add 5 c.c. hydrochloric acid, evaporate once more (no nitrous fumes ought to escape now), add 1 c.c. concentrated hydrochloric acid and 100 c.c. hot water; pass through a small filter and wash with hot water. The insoluble residue may be dried, ignited, and weighed. It may contain, besides silicic acid and silicates, the sulphates of barium, lead, and even calcium, whose sulphur, as being useless, is purposely neglected. (If this residue is not to be estimated, it need not be filtered off, and the next step, the elimination of the iron, may be taken without removing the silica, etc.) The filtrate and washings are saturated with ammonia, avoiding a very large excess of it; the mixture is kept at a moderately warm temperature for about ten minutes (at the expiration of which time it ought still to smell of ammonia very distinctly, not merely faintly), and the precipitated ferric hydrate is filtered off while the liquid is still hot. For this purpose funnels must be used, made at an angle of exactly 60°, whose tube is not too wide and is *completely* filled by the liquid running through; or else a Piccard's tube (*cf.* above, p. 92), or a filter-pump is employed. The filtering-paper must be sufficiently dense, but should act rapidly; the filter must be adapted to the funnel so that no air-channel is left between paper and glass. The hot liquid is first decanted from the ferric hydrate, and the latter is then washed on to the filter with boiling water. The washing is continued with hot water in such manner that each time the whole precipitate is thoroughly churned up and no channels are formed in the mass. When acting on these instructions, the whole operation can be performed in from half to one hour, and no trace of sulphuric acid is retained in the precipitate. The total bulk of the filtrate and washings need not exceed 200 or 250 c.c., which saves concentrating the liquid by evaporation. The end of the washing is indicated by the fact that 1 c.c., on adding barium chloride, shows no opalescence even after a few minutes. (It is, however, best in important cases to test the iron precipitate for sulphur by drying it, detaching it as well as possible from the filter, fluxing with pure sodium carbonate, dissolving in hot water, acidulating and adding $BaCl_2$.)

The clear liquid, which now contains all the sulphuric acid combined with ammonia, is acidulated with pure hydrochloric acid in very slight excess, heated to boiling, the burner removed, and 20 c.c. of a 10-per-cent. solution of barium chloride, previously heated, is slowly poured in. This quantity, which suffices in any case for 0.5 g. pyrites, is roughly measured off in a test-tube provided with a mark, and is heated in the same tube. After precipitation, the liquid is left to stand for half an hour, when the precipitate should be completely settled. The clear portion is now decanted, and the washing continued by decantation with boiling water, as mentioned on p. 93, where the mode of igniting the precipitate is also described. The ignited precipitate should be a perfectly white and loose powder, 1 part of which is equal to 0·1373 sulphur.

The accuracy of this method and its complete accordance (in the case of pure ores) with the fusion method of Fresenius have been proved by Pattinson (*J. Soc. Chem. Ind.*, 1890, p. 21), who points out how much more convenient is the former than the latter. Lunge (*Z. angew. Chem.*, 1905, p. 1656) and Lunge and Stierlin (*ibid.*, p. 1921) have again confirmed it. *Cf.* also Lunge (*ibid.*, 1906, p. 1854).

Kuster and Thiel (*Z. anorg. Chem.*, xix. p. 97) erroneously assume that the ferric hydrate cannot easily be washed by my method so as to remove all sulphate (which is refuted by hundreds of students who have carried out this method in my laboratory, and thousands of chemists elsewhere). They therefore propose to precipitate the barium sulphate without filtering off the ferric hydrate and to remove the latter subsequently by several hours' digestion with hydrochloric acid; or else to prevent the precipitation of ferric salts along with the barium sulphate by the addition of a large quantity of ammonium oxalate. Both methods take much more time than mine, without any gain in accuracy, as I have shown in *Z. anorg. Chem.*, ix. 454, and again, xxi. p. 194. This is confirmed by Herting (*Z. angew. Chem*, 1899, p. 274).

According to Heidenreich (*Z. anorg. Chem*, xx. p. 233) the contamination of barium sulphate by iron salts can be avoided by reducing the ferric sulphate to ferrous sulphate by means of zinc and preventing the excess of air and light during the precipitation. Herting and Lehnardt (*Chem. Zeit.*, 1899, No. 75) effect the same purpose much more quickly by employing stannous chloride in lieu of zinc. Gyzander (*Chem. News*, 1906, xciii. p. 213) employs hydroxylamine for the same purpose.

Noaillon (*Z. angew. Chem*, 1897, p. 351) proposes to avoid the filtration of the ferric hydrate by diluting the liquid to a certain mark, filtering, and employing a portion of the filtrate for the precipitation with barium chloride; but this method introduces more than one error and must be rejected.

Johnston and Adams (*J. Amer. Chem. Soc.*, 1911, pp. 824 *et seq.*) discuss in great detail the occlusion of foreign salts in the barium sulphate precipitate, and describe their method for an exact estimation of sulphates, which is of no special interest in our case.

Sodium peroxide is proposed for the decomposition of pyrites by Hempel, Hohnel (*Arch. Pharm.*, 1894, p. 222), and Glaser (*Chem. Zeit.*, 1894, p. 1448).

In lieu of the estimation of sulphuric acid by weight, some chemists prefer *titration* by means of a standard solution of barium chloride. This was first proposed by Wildenstein (*Z. anal. Chem.*, i. p. 432), and afterwards, especially for the analysis of pyrites, by Teschemacher and Smith (*Chem. News*, xxiv. pp. 61, 66; *cf.* also Glendinning and Edger, *ibid.*, p. 140). Although this process, notwithstanding some assertions to the contrary, is most certainly no more accurate than the gravimetric process, and in most hands is less so, and is not used by many chemists in important cases, we shall take this opportunity of describing the estimation of sulphates by titration with barium chloride in its simplest form, such as is used at some works in testing black-ash, etc.; it is also used sometimes in testing pyrites, blende, burnt-ore, etc., for purposes where no great accuracy is required.

The liquid is brought to the boil in a porcelain dish, barium-chloride solution is added from a burette; from time to time a few drops are taken out with a glass tube, passed through a miniature filter on to a glass plate resting on a black background, upon which a number of drops both of dilute sulphuric acid and of barium chloride have been put. If the filtrate still gives a cloudiness with a barium-chloride drop, easily visible on the black ground, the little filter is thrown back into the dish, more barium-chloride solution is added from the burette, another test is made, and so forth. The end is attained when a filtered drop gives an extremely slight cloudiness both with a drop of barium chloride and with one of sulphuric acid. The work is very much expedited by the following contrivance, proposed by Wildenstein and shown in Fig. 7. The acidulated solution is poured into a vessel, A, made of a bottle by removing the bottom, or a small tubulated jar, through whose cork passes a bent tube, B, provided at the lower end with a pinch-cock, *l*, at the upper end with a bent-down funnel, *f*. The latter (which must be bell-shaped) is closed by two disks of filtering-paper and a piece of linen gauze tied over all; and the liquid must cover the whole tube. This arrangement permits of withdrawing at will small filtered samples of a few drops each, which are run into a test-tube and tried with a drop of barium-chloride solution. It must, of course, not be omitted first to run a few cubic centimetres out of the tube B and back into the jar A before taking the sample for testing; and the contents of the test-tube must be always put back into A, not to waste too much substance. If by accident the point of finishing the reaction has been overstepped, one or more cubic centimetres of titrated sulphuric acid are put in and are afterwards deducted from the result.

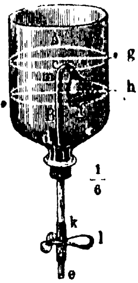

FIG. 7.

C. and J. Beringer effect the titration by barium chloride after addition of sodium acetate and acetic acid (*Chem. News*, lix. p. 41).

Various other volumetric methods for the estimation of sulphates, by Carl Mohr, Ad. Clemm, Wildenstein (2nd method), Schwarz, and Pappenheim, are described in the treatises of Fresenius and Mohr; but they are more complicated and not more accurate than the direct titration with barium chloride as just described. We therefore mention only one method of this kind. This is the method proposed by Wilsing (*Chem. Ind.*, 1886, p. 25), a slight but apparently useful modification of those just mentioned. He precipitates a neutral solution of the sulphate or solution containing such, boiling in a porcelain dish, with a 4-per-cent. barium-chloride solution of known strength; he then adds a few drops of an alcoholic solution of phenolphthalein and a 2-per-cent. solution of sodium carbonate: as soon as the last part of barium chloride has been precipitated as carbonate the colour turns red, so that the soda used is a measure for the sulphate originally present. If the solution to be tested is either acid or alkaline, it must be made neutral by sodium carbonate or hydrochloric acid, phenolphthalein being used as indicator here as well.

L. W. Andrews (*Amer. Chem J.*, 1889, p. 567, and *Chem. Zeit. Rep.*, 1889, p. 39) proposes the following method for estimating sulphuric acid combined with bases:—The solution is diluted till it contains no more than 2 per cent. SO_3, is almost neutralised and brought to a boiling heat. Now a solution of pure barium chromate in hydrochloric acid is added, and then ammonia, the excess of which is removed by boiling. The solution is filtered while hot and is washed at once. Now a quantity of chromic acid, equivalent to the sulphuric acid originally present, will be in solution; this is estimated by adding potassium iodide and strong hydrochloric acid, and titrating with decinormal thiosulphate solution (1 c.c. = 12·85 mg. I = 2·662 mg. SO_3). It is claimed that this operation is more quickly performed than the gravimetric process, and is at least as accurate; but both of these assertions are doubtful.

Similar methods are described by Reuter (*Chem. Zeit.*, 1898, p. 357) and Marboutin and Moulinié (*Chem. Centr.*, 1898, i. p. 218).

Several methods have been proposed for estimating the *available sulphur* of sulphur-ores—that is, that portion of it which passes into the chambers in the shape of SO_2 and SO_3. Thus W. G. Mixter (*Amer. Chem. J.*, ii. p. 396) burns the pyrites in a current of oxygen, and passes the vapours into bromine-water containing some hydrochloric acid and an excess of bromine. A similar process is recommended by Zulkowsky (Wagner's *Jahresber.*, 1881, p. 160), both for testing pyrites and spent oxides of gas-works. The latter is always contaminated with sawdust, tarry matters, and variable quantities of lime, which retains part of the sulphur in burning, whence an estimation of the total sulphur is quite useless for practical purposes. The process takes place in a combustion tube (Fig. 8), 2 ft. long, narrowed at *a*, and drawn out at the end into a long tube, not too thin, and bent downwards. Between *a* and *b* there is a layer of platinised asbestos (see below), 8 to 10 in. long, and at a distance of 3 or 4 in. from this a porcelain boat with about 0·4 g. of spent oxide or pyrites. The end of the tube at *k* is connected with an oxygen gas-holder. The absorption of the vapours takes place in the two 3-bulb tubes *c* and *d* ($5\frac{1}{2}$ in. high) and the tube *e*, filled with glass-wool. The absorbing-liquid is made by dissolving 180 g. caustic potash (purified with alcohol from sulphate) in water, adding 100 g. bromine, taking care to keep the mixture cool, and diluting to 1000 c.c. Thirty c.c. of this suffice for estimating 0·5 g. sulphur. The tube *e* ought also to be moistened with it. First heat the portion of the tube between *a* and *b*, passing moist oxygen through it at the same time; then heat the boat from the right to the left; lastly the tube, up to the place *f*. The current of gas must be much stronger than for an organic analysis, lest any sulphur should escape unburnt, but not strong enough to draw off any SO_3 unabsorbed. So long as any dew appears at *h*, it must be

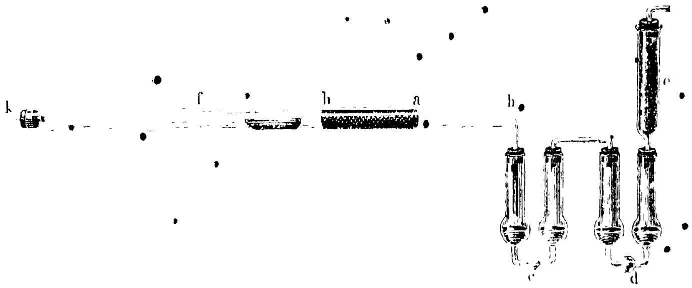

FIG. 8.

driven into the receiver with a Bunsen burner. When this ceases (usually in about an hour), the experiment is finished. The receivers are then taken off, washed out, and the acid remaining in *h* is recovered by aspirating water several times through it. All the liquids are united, supersaturated with hydrochloric acid in order to decompose the potassium hypobromite, heated, concentrated if necessary, and the sulphuric acid is precipitated by barium chloride in the usual manner (or, more conveniently, the receivers are charged with hydrogen peroxide, free from sulphuric acid, and are retitrated after the end of the operation.

Dennstedt and Hassler (*Z. angew. Chem.*, 1906, p. 1668) employ a similar method. Some remarks upon this are made by Lunge (*ibid.*, p. 1854). Heczko (*Z. anal. Chem.*, i. 748) obtained good results with it.

Nitchie (*J. Soc. Chem. Ind.*, 1912, p. 30) employs a similar process for the estimation of sulphur in roasted blende.

Jannasch (*J. prakt. Chem.* [2], xl. p. 237) heats pyrites in a mixture of air or oxygen and nitric-acid vapours; the vapours of SO_2 and SO_3 are absorbed in bromine-water. [It must not be forgotten that in the presence of nitric acid the barium sulphate is never free from nitrate, and that hence all nitric acid must be removed previously. I would, therefore, propose to use in that class of processes hydrogen peroxide as an absorbent, which is very efficient and requires no special precautions; in this case the acids absorbed can be estimated by titration with the standard alkali.]

Graeger (*Dingl. polyt. J.*, ccxli. p. 53; *Fischer's Jahresber.*, 1881, p. 161) heats pyrites with reduced metallic iron, decomposes the FeS formed by dilute hydrochloric acid, and titrates the H_2S evolved by passing it into a solution of iodine. This method has been again proposed by Treadwell (*Berl. Ber.*, xxiv. p. 1937, and xxiv. p. 2377) and by Eliasberg (*Z. anal. Chem.*, 1899, p. 240), but it does not seem to be practically employed.

Expeditious assays of pyrites have been proposed in many ways, but none of them is sufficiently accurate to be employed for estimating the sulphur in fresh pyrites, and some of them are not even accurate enough for testing the sulphur remaining in *burnt-ore* (pyrites cinders).

The so-called *mechanical pyrites assay* of Anthon (*Dingl.*

polyt. J., clxi. p. 115) is too rough and unreliable even for very simple purposes. (*Cf.* 1st ed. of this work, i. p. 108.)

In the Freiberg works 1 g. of finely ground pyrites is mixed with 2 g. sodium carbonate and 2 g. saltpetre: the mixture is fluxed in a small iron dish in a red-hot muffle-furnace, dissolved in hot water and filtered into a beaker in which there is hydrochloric acid by saturating the soda in excess. Then the filtrate is brought to boiling, and the sulphuric acid estimated by a standard solution of barium chloride, preferably by Wildenstein's method (*suprà*, p. 98). Liebig (Post's *Tech. chem. Analyse*, 2nd ed. i. p. 677) recommends this method as a quick and easy one, where no great accuracy is required.

In the method of Pelouze (*Comptes rend.*, liii. p. 685; *Ann. Chim. Phys.* [3], lxiii. p. 415) the finely powdered pyrites is mixed with chlorate of potash, common salt, and an exactly weighed quantity of sodium carbonate, and ignited, which can be done in an iron spoon. The fluxed mass is dissolved in water, filtered, the residue is washed, and the soda not converted into sulphate is estimated alkalimetrically. This process continued to be recommended in French treatises, although its inaccuracy was established and the sources of error partly demonstrated by many chemists, such as Barreswil, Bottomley, Bocheroff, Lunge, and especially Kolb (*Notes sur l'Essai des Pyrites de Fer*). Kolb found the sources of error on the one hand in the formation of sodium silicate, on the other hand in the decomposition of potassium chlorate in the presence of ferric oxide into chlorine, oxygen, and caustic potash. New experiments made in my laboratory by Mr Rey have equally proved the method to be wrong, even if the "constant error" of 1 to 1½ per cent., admitted by Pelouze, is taken into account. A principal objection is the difficulty of evading the mechanical loss by spurting in the fluxing process.

This fault is avoided in the plan proposed by Kolb (*J. Pharm. Chim.* [4], x. p. 401), which, however, is only intended for testing *burnt-ore*. Kolb mixes 5 or 10 g. of this with 5 g. pure sodium carbonate and 50 g. of cupric oxide, heats about fifteen minutes in an iron capsule to a dark red heat, with stirring, lixiviates the melted mass, and estimates the unconsumed soda volumetrically. The trials made in my laboratory showed that there is no spurting, but that the heating must not be prolonged too much, in order to avoid the formation of silicates. The lixiviation of the large bulk of cupric and ferric oxide is tedious, and the method is somewhat costly, as it requires 50 g. of cupric oxide for each test, nor are the results very satisfactory (see below).

A much better method for testing burnt-ore was proposed by J. Watson (*J. Soc. Chem. Ind.*, 1888, p. 305). Two or 3 g. of pyrites cinders are mixed with 1 or 2 g. of sodium bicarbonate of known titre; the mixture is heated in a nickel, porcelain, or platinum crucible by means of a small Bunsen flame for five or ten minutes, stirred up, heated once more for fifteen minutes with a somewhat stronger flame, treated with hot water, filtered and washed. The solution is titrated with hydrochloric acid and methyl-orange; the loss of titre in comparison with the original one is equal to the sulphate formed. The escaping carbonic acid keeps the mass porous; there is no spurting, and the lixiviation of the small bulk of the mixture is easy and expeditious.

Experiments made in my laboratory (*Z. angew. Chem.*, 1892, p. 447) showed that Watson's method yielded results closely agreeing with those obtained by accurate gravimetrical methods, whilst the method of Pelouze, even with burnt-ore, yielded too low results, and that of Kolb was not more reliable. But it was found that special precautions, as now described, must be observed in order to yield accurate results. 3·200 g. of the finely ground samples are mixed with 2·000 g. sodium bicarbonate (of known alkalimetrical titre), and heated in a nickel or iron crucible; a platinum crucible easily leads to overheating. The heating is continued for ten or fifteen minutes with a very small flame, then another fifteen minutes with a strong flame, but without fusing the mass. The crucible must be kept covered and the mass must not be stirred; it should in the end be red-hot, and after cooling black and porous. It is boiled in a porcelain dish with water, adding the same volume of neutral solution of sodium chloride. This is an essential improvement, as without this addition some oxide of iron invariably passes through the filter, and makes the following titration by methyl-orange almost impossible. The filtered solution is titrated with standard acid. The difference between the original titre of bicarbonate and that now found shows the sulphur, 1 c.cm. normal acid indicating 0·5 per cent. S. In the presence of a somewhat considerable quantity of zinc this method does not answer.

It cannot be our purpose in this place to describe all the methods for testing burnt pyrites for sulphur; we refer in that respect to Lunge's *Technical Chemists' Handbook* (1910), and Lunge's *Technical Methods of Chemical Analysis*, translated by C. A. Keane (1908).

We here only mention, as not yet found there, a new method by Hohorst (*Abstr. Amer. Chem. Soc.*, 1911, p. 2051), founded on the reduction of the sulphur compounds to H_2S by means of Al and Fe, and absorbing the H_2S in a solution of cadmium acetate.

Magnetic pyrites (*pyrrhotite*), Fe_7S_8, is sometimes present, especially in some kinds of American pyrites. As that ore yields its sulphur very imperfectly in ordinary pyrites-kilns, its estimation may become important. Cone (*J. Amer. Chem. Soc.*, xviii. p. 404) effects this by grinding the ore so that all passes through a 60-mesh sieve (not more finely!), spreading the powder on a sheet of glazed paper, applying a magnet to this, removing the mechanically adhering pyrites by gently knocking the magnet and separately brushing off the pyrrhotite after putting on the anchor. This is repeated five or six times, and the sulphur estimated in the separated portions.

Marcasite and pyrites can be distinguished by the easier decomposition of the former when boiling with a solution of ferric salt. This behaviour has been studied in detail by H. N. Stokes (*Bulletin U.S. Geol. Surv.*, No. 186); but it is of no practical importance for technical analysis.

Estimation of other constituents of pyrites.—Usually it is sufficient to estimate the sulphur in a pyrites whose nature is otherwise known. If, however, the pyrites is of unknown composition, its value for acid-making can only be estimated by a complete determination of all its constituents according to the rules of mineral analysis. If it contains, for instance, *calcium carbonate*, this on burning will retain its equivalent of sulphuric acid equal to 0·32 per cent. S for each per cent. $CaCO_3$; if *calcium sulphate* is present from the first, its sulphuric acid has to be deducted from the whole quantity of sulphur found. If *lead* has been found, its equivalent of sulphur must be considered as practically lost; and the same is the case with *zinc*—because the sulphates of both metals are hardly or not at all decomposed at the temperature of a pyrites burner. In France half of the S combined with Zn is considered as lost, = 0·245 per cent. S per 1 per cent. Zn (for copper they reckon 0·505 per cent. S per 1 per cent. Cu as lost). Frequently *arsenic* will also have to be sought for; and even *silica* may be of importance—firstly, because in the presence of much silica "explosive" properties of the pyrites must be feared (see p. 80), and secondly, in the case of cupreous pyrites, because silica lessens the value of the cinders. Even *silver* and *gold* are sometimes sought for (cf. *Chem. News*, xxvi. p. 63; xxxiv. pp. 94, 132, 152, 172); but it cannot be said that the quantities hitherto found have any influence on the commercial value of pyrites.

Treadwell and Koch (*Z. angew. Chem.*, 1903, p. 173) describe the estimation of *carbon* in pyrites, especially the "coal brasses." This can be done by the ordinary method of elementary analysis, but better by the method of Corleis (dissolving in chromic acid, and absorbing the CO_2 formed by soda-lime), for which they introduce some convenient modifications. The estimation of *selenium* has been mentioned, *suprà*, p. 55.

It is not our object here to treat of the estimation of all these substances, nor that of the *copper* which, in the majority of cases, represents a large portion of the value of pyrites.[1] We make an exception only with *arsenic*, because special methods for estimating this in pyrites have been worked out which are not found in the ordinary text-books.

The process employed at Freiberg is that used by Reich, and is as follows:—Digest about 0·5 g. of finely pulverised pyrites in a porcelain crucible, covered with a watch-glass, with concentrated nitric acid at a gentle heat, until the residue assumes a lighter colour and the separated sulphur has turned a pure yellow. After decomposition, heat the crucible on a sand-bath to get rid of the excess of acid, but not to dryness. Add

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[1] For these substances, see Lunge's *Technical Chemists' Handbook*, published by Gurney and Jackson, 1910; also a very extensive paper by Westmoreland, *J. Soc. Chem. Ind.*, 1886, p. 31, and criticisms on the same, p. 277; and Lunge's *Technical Methods of Chemical Analysis*, English Translation by Keane, published by Gurney and Jackson, 1908, vol. i. pp. 285 *et seq.*

4 g. of sodium carbonate, dry completely on the sand-bath, add 4 g. of potassium nitrate, and heat the mass until the contents of the crucible have been in quiet fusion for ten minutes. Extract the cooled mass with hot water and filter; the filtrate contains all the arsenic as sodium arseniate. Acidify with a little nitric acid, keep for two hours on a sand-bath to get rid of the carbon dioxide, add a sufficient quantity of a solution of silver nitrate, and neutralise carefully with dilute ammonia. The reddish-brown precipitate of silver arseniate is filtered, washed, dried, taken off the filter as well as possible, the filter is incinerated in a muffle, the precipitate put to it, a sufficient quantity of assay lead is added, and the silver estimated by cupellation. One hundred parts of silver correspond to 23·15 of arsenic.

Leroy M. M'Cay has modified and greatly simplified this method (*Chem. News*, xlviii. p. 7) by estimating the excess of silver used by Volhard's method. Later on (*Amer. Chem. J.*, viii. No. 2) the same author recommends as preferable another plan, namely dissolving the Ag_3AsO_4 in dilute ammonia, and either estimating the silver by Volhard's volumetric method (precipitation with ammonium thiocyanate), or evaporating, drying, and weighing the total in a thin platinum dish. If the arsenic is to be precipitated as pentasulphide, which is otherwise a tedious operation, M'Cay recommends (*Amer. Chem. J.*, ix. No. 3, and x. No. 6) to place the solution in a flask with a well-fitting stopper, acidify with HCl, and dilute with freshly boiled water till the flask is nearly full, pass in H_2S to saturation, insert and fasten down the stopper, and place the whole in a water-bath for an hour. At the end of that time all the arsenic will be precipitated as pentasulphide, As_2S_5, containing no free sulphur.

Clark (*J. Soc. Chem. Ind.*, 1887, p. 352) recommends the following method as especially adapted for estimating very small quantities of arsenic in pyrites rich in sulphur:—Mix 3 g. of pyrites in a platinum crucible with four times as much of a mixture of calcined magnesia and sodium hydrate, heat for about ten minutes over a moderately low Bunsen flame, extract the shrunk mass with boiling water, acidify the solution with hydrochloric acid (which evolves much H_2S), boil for a few minutes, and saturate with H_2S, when all the arsenic will be thrown down as sulphide; wash the precipitate, extract the sulphide of arsenic with ammonia, evaporate the solution to dryness, dissolve in strong nitric acid, and estimate the As as ammonio-arseniate of magnesia, or else by silver solution as above described. Or else the calcined mixture, after neutralising it with HCl, as above mentioned, is reduced by cuprous chloride, and the liquid is slowly distilled into water, repeating this operation twice with strong HCl, which will cause all the arsenic to pass over as $AsCl_3$, which can be either precipitated by H_2S or titrated by iodine. Clark points out the necessity of carefully testing all the reagents employed for arsenic, of which he had found as much as 0·02 per cent. even in commercial caustic soda.

Nahnsen's process (*Chem. Zeit.*, xi. p. 692; abstr. *J. Soc. Chem. Ind*, 1887, p. 564) does not offer any special advantage. The process described in detail by H. Fresenius (*Z. anal. Chem.*, 1888, p. 34) is no doubt very accurate, but lengthy and troublesome.

Blattner and Brasseur (*Z. angew. Chem.*, 1898, p. 262) give exact instructions for estimating arsenic in pyrites, both in the wet and dry methods.

Vilstrup (*Chem. Zeit.*, 1910, 350; *Chem. Soc. Abstr.*, 1910, ii. p. 458) estimates in pyrites the sulphur and iron by Lunge's method. For the estimation of arsenic he moistens 12·5 g. of the powdered ore in a large beaker with 10 c.c. of water and 1 c.c. of sulphuric acid, adds strong nitric acid until there is no further effervescence, boils the liquid to a paste and treats the residue with boiling water. If the residue is not white, the liquid is decanted and the insoluble mass boiled with aqua regia. This is then evaporated and the residue transferred to the main solution, and the whole is diluted to 250 c.c. The solution is then passed through a dry filter; the residue is washed and tested for lead by boiling with ammonium acetate; excess of sulpnuric acid reprecipitates the lead. Two hundred g. of the filtrate (= 10 g. of the sample) are treated with hydrogen sulphide. The precipitate, consisting of copper and arsenious sulphide, is treated with ammonium carbonate; this dissolves the arsenic, which is then reprecipitated by adding dilute sulphuric acid and passing H_2S in. The As_2S_3 is collected in a Gooch crucible, washed with alcohol and carbon disulphide, dried at 100° and weighed. The copper sulphide is freed from admixed sulphur and traces of antimony sulphide by boiling with sodium sulphide, and then washed and burned to oxide. The filtrate from the copper arsenic precipitate is diluted to 500 c.c., 50 c.c. (= 1 g. sample) are boiled, oxidised with nitric acid and, after adding an excess of ammonium chloride, precipitated with ammonia. As the iron precipitate retains zinc, it should, after washing, be redissolved in hydrochloric acid and, after neutralisation, boiled with ammonium acetate or nitrite. The united filtrates then contain all the zinc. After adding ammonia and heating to boiling, any Ca and Mg are precipitated by adding a like ammonium carbonate and phosphate; the liquid should then be stirred for half an hour. From the filtrate, the zinc-ammonium phosphate is recovered by boiling off the NH_3, and finally converted by ignition into zinc pyrophosphate and weighed as such. If the colour should not be pure white traces of Ni or Co phosphate may be present. In such cases the filtrate from the iron is acidified with acetic acid and treated with H_2S. After twenty-four hours the precipitate is collected and treated with cold *N*-hydrochloric acid; the zinc dissolves, and the Ni and Co are not affected. From the filtrate the zinc is then recovered as pyrophosphate in the usual way. Hattensaur (*Chem. Centr.*, 1911, i. p. 1373) recommends this process.

3. ZINC-BLENDE.

This mineral is now the principal zinc-ore. Previously to reducing the zinc, the blende must be roasted in order to convert it into ZnO, and this process was formerly carried out without taking any care to deal with the enormous quantities of SO_2 formed. Sanitary legislation at last interfered with this procedure, which of course laid waste all the country round the zinc-works, and compelled measures for dealing with the noxious gases. Part of these are now used for the production of liquid sulphur dioxide (*cf.* Chapter IV.); mostly, however, they serve for the manufacture of sulphuric acid, so that blende has now become one of the more important raw materials for this purpose. The historical development of this industry will be related in Chapter IV.

Blende occurs in large quantities; for instance, in Silesia, Westphalia, Rhineland, Saxony, Austria, Belgium, Wales, the Isle of Man, Spain, Italy, France, the United States, in nearly all of which localities it is utilised for the manufacture of sulphuric acid.

Pure blende, ZnS, contains 32·9 per cent. S, and 67·1 per cent. Zn. The commercial ore is, of course, always impure. We quote the following analyses, by Minor (*Chem. Zeit.*, 1889, p. 1602), of Rhenish blende:—

S	30·24	27·94	22·11	21·05
Zn as ZnS	22·73	27·17	34·46	31·16
Zn in other combination	5·03	4·75	5·83	6·65
Fe	15·98	13·12	2·06	2·33
Gangue (by diff.)	21·02	27·02	35·54	38·84

Drasche analysed a blende from Carinthia: ZnS 68·41 per cent.; PbS 4·55; FeS_2 2·05; $ZnCO_3$ 2·40; $CaCO_3$ 8·93; $MgCO_3$ 10·62; Al_2O_3 0·63; gangue (principally quartz) 2·32 per cent.

Pennsylvanian blende, according to F. A. Genth:—Sulphur 32·69 to 33·06 per cent.; Zinc 66·47; Iron 0·38; Cobald 0·34.

Jurisch (*Schwefelsaurefabrikation*, p. 61) quotes analyses of various descriptions of blende, burnt by the Chemische Fabrik, Rhenania, with sulphur contents varying from 18·40 to 32·20, and zinc from 14·90 to 50·22 per cent.

Haenisch and Schroeder (*Chem. Ind*, 1884, p. 118) quote the contents of Silesian blende = 23 to 37 per cent. S, also an inferior blende = 8 to 21 per cent. S.

Blende frequently contains cadmium and mercury. The latter occurs in Rhenish blende to the extent of only = 0·02 per cent., but in Spanish (Aviles in Asturia) = 0·135 per cent.

According to direct information from the Rhenania Chemical Works at Stolberg, the sulphur contents in the blende roasted there ranges between 20 and 30 per cent.; on the average 25 to 28 per cent. Iron does not do any harm, but lime retains its equivalent of S as $CaSO_4$. Lead affects the duration of the roasting-beds; it is partially volatilised with a little silver, and reappears in the flue-dust, the towers, and chambers. Mercury and fluorine are also volatilised and act very injuriously on the platinum vessels used for concentration. Arsenic generally occurs in blende in such extremely slight quantities that the acid made from it may be considered as technically pure.

In our last edition it is stated that the sulphuric acid works recently refuse to accept blende containing *fluorides*. Truchot (*J. Soc. Chem. Ind.*, 1911, p 207) states that blende nearly always contain calcium fluoride, ranging from a few grammes to 250 to 300 g. per 100 kg. Lead is attacked notably by sulphuric acid of 53° B. containing small quantities of hydrofluoric or hydrofluosilicic acids, and it appears certain that the life of the chambers and more so that of the first tower, and that of the Glover tower, must be considerably shortened by the use of blende containing fluorine. Fluorine compounds also attack the silicious lining of the Glover tower.

Delplace (Ger. P. 200747) removes the fluorides from blende by heating the ground mineral with sulphuric acid, if necessary with additions of silica in the form of powdered glass or quartz; the fluorine compounds are recovered and utilised.

Jensch (*Z. angew. Chem.*, 1894, p. 59) shows by analyses that the sulphur in *roasted blende* is mostly contained therein in the shape of ferrous sulphide; when roasting down to 2 per cent. S, no ZnS is present, and it is therefore quite unnecessary to drive the roasting down to 0·5 per cent. S, as is sometimes demanded.

Statistics.—The production of blende in Prussia in 1890 amounted to 362,464 tons; Belgium in 1889 to 12,376 tons; France and Algiers in 1887 to 13,800 tons; Spain in 1885 to 2488 tons. In 1908 435,750 tons blende was worked in Germany for the production of sulphuric acid and liquid sulphur dioxide.

Analysis of Zinc-blende.—The sulphur is estimated by the wet method as described, p. 96. In the *cinders* from blende the same method must be employed since the dry methods, *e.g.*, Watson-Lunge's (p. 104), in this case give quite wrong results. Details respecting this and the other constituents of zinc-blende are found in Lunge's *Technical Chemists' Handbook* and Lunge-Keane's *Technical Methods of Chemical Analysis.*

A rapid method for the *determination of sulphur in roasted blende* is described by Nitchie in *J. Soc. Chem. Ind.*, 1912, pp. 30 *et seq.* It consists in heating the sample, preferably in a boat, by means of an electric tube furnace, in a current of air to about 1000°, absorbing the resulting oxides of sulphur in an excess of standard alkali solution and titrating the excess, phenolphthalein being used as an indicator. This method (which, according to Nitchie, does not answer for raw ores) takes less than ten minutes from taking the sample to completing the titration, and may be entrusted to boys with but little training in chemical manipulation.

Hassreidter (*Z. angew. Chem.*, 1906, p. 137) tests roasted blende (1) for zinc sulphate, by extracting with warm water and estimating the zinc in the solution by Schaffner's method; (2) for sulphides, by boiling with a solution of 39 g. tin in 1 litre concentrated hydrochloric acid, and passing the gases containing H_2S through a ten-bulb tube charged with a solution of bromine in hydrochloric acid, where all the sulphur is retained as H_2SO_4; the latter is found by precipitation with barium chloride, after previously removing the excess of bromine and approximately neutralising with sodium carbonate.

4. OTHER METALLIC SULPHIDES—NOXIOUS VAPOURS.

Pyrites proper has hardly any other application than that for sulphuric-acid making, and it is obtained almost exclusively for this purpose. In the case of cupriferous pyrites the sulphur constitutes only a portion, but a very considerable one, of its value. The working of poor copper-ores would not pay, apart from the noxious effect of the gas produced in calcining the ore, unless the price of the ore were very moderate; and this is only possible by the acid-makers paying on their part for the ore, which they can well afford, as most kinds of cupreous pyrites behave very well in the burners, and yield quite as much acid in proportion to their percentage of copper as the non-cupreous ores. The case of zinc-blende is now similar to that of cupreous pyrites.

The case is different with most other sulphuretted ores occurring in smelting operations, such as *galena*, the many *mixed ores* containing blende and galena, besides iron- and copper-pyrites; the richer *copper-pyrites* themselves, and, lastly, the intermediate products, "*coarse metal*," "*matte*," etc. These, for their metallurgical utilisation, equally require a calcination evolving sulphur dioxide; but the matter is very different here from what it is with a good pyrites, whether it be pure iron-pyrites or containing a few per cent. of copper. On the whole, all those ores and metallurgical products are much poorer in sulphur than ordinary good pyrites; and for this reason they are less easily calcined in such a manner as to allow of utilising the gas, because the evolution of heat by the combustion of their own sulphur is not sufficient to maintain the process energetically. An external stimulus was required before smelting-works would seriously attempt to utilise the sulphur dioxide contained in the gas from calcining the ores; and this proved to be the damage and nuisance caused by the *noxious vapours* all round the works. The claims for damages, the law-suits, and the measures taken by the authorities at last made it impossible in many places for the works to go on in the old way; and although it appeared at first as if the sulphurous acid could not be condensed at all in this case, or only at a loss, practice has now succeeded in fulfilling the task in most (but not in all) cases, principally by the construction of improved burners, which will be described in Chapter IV. It would undoubtedly be too much to say that the task had been solved in all its parts; the success has mostly been only partial. In many cases where an ore could not possibly have been calcined so as to utilise the gas, mixing of it with others has been resorted to. Thus the Halsbrücke works, near Freiberg, roast galena and blende mixed with pyrites; and in 1870 they made 8000 tons of sulphuric acid from the gas.

In reference to the sulphur dioxide escaping as noxious vapour, Leplay (*cf.* Percy, *Metallurgy*, 1862, i. p. 337) mentions that in South Wales annually 46,000 tons of sulphur escaped into the air as sulphur dioxide, together with arsenic, fluorine, lead, and zinc compounds, in spite of the condensing-chambers. In fact, the country round Swansea was stripped of all vegetation. At Freiberg the works in 1864 paid upwards of £2750 damages on account of their vapours, in 1870, after better condensation had been effected, only £239. It should not be forgotten that sulphur dioxide occurs in very large quantity, although in a much more dilute state, in all coal-smoke, and consequently in the atmosphere and the rain-water of all large towns, and that the most perfect "smoke-combustion" cannot do away with this. Much more injurious than the vapours escaping through high chimneys, which are soon diluted with air, is the smoke from brick-works, coke-ovens, and other fires which emit their smoke at a low height above the ground. Mr Fletcher has calculated that at St Helens the acids escaping amounted:

From fire-gases . . .	to 800	tons per week.
„ copper-works . .	„ 380	„ „
„ glass-works . .	„ 180	„ „
„ alkali-works . .	„ 25	„ „

Similar calculations have been made by Mr Hasenclever (*Chem. Ind.*, 1879, p. 225), who has given strong proof of the damage done by coal-smoke alone.

According to the *28th Alkali Report* (for the year 1891), p. 19, the quantity of acid gas which at that time escaped into the air at St Helens, calculating HCl as its equivalent of sulphur acids, was as follows:—

	Tons sulphur per annum	
From Copper and Lead smelting works . . .	11,480	19,313
„ Glass-works	7,500	
„ Polishing-powder works	333	
„ Coal-burnt ($1\frac{1}{2}$ per cent. of 1,040,000) . . .		15,600
„ Chance-Claus process		620
„ Sulphuric-acid chambers	173	575
„ Alkali-works	402	
Total . .		36,108

This is the equivalent of 72,216 tons SO_2 or 110,586 H_2SO_4, of which the alkali-works contribute only $1\frac{1}{2}$ per cent. Since all this is given off from an area of about 3 sq. miles, each square mile at St Helens received the equivalent of 12,036 tons of sulphur, against 11 tons in summer or 44 tons in winter on a square mile in London.

In Chapter IV. we shall deal with the various attempts at utilising, or at least rendering innocuous, the acid gases given out in calcining ores, and we shall here enumerate only the various classes of ores or waste substances coming under the head of causing "noxious vapours," such as might serve for the manufacture of sulphuric acid (apart from zinc-blende, *cf.* p 109).

Copper-pyrites and mixtures of this with blende, galena, etc., are roasted in several places in kilns so as to utilise the SO_2 in acid-chambers—at Chessy near Lyons, at Oker in the Harz, at Manzfield, at Swansea. At the Altenau silver-works near Clausthal, in 1872, 228 tons of vitriol of 106° Tw. were made from copper-pyrites (and 314 tons from lead-matte, Wagner's *Jahresber.*, 1874, p. 276). At Freiberg the Mulden and Halsbrücke works proceed in the same way; but they only utilise ores and products pretty rich in sulphur for vitriol-making.

The following particulars respecting the materials burned at the Government works at Oker in 1901 have been communicated to me from an official source. The ores are:—

	Lumps.		Total
	Tons.	Tons	Tons.
Copper-ores, No. 1 .	1,205	895	2,100
" 2 .	4,095	88	4,183
" 3 .	1,417	73	1,490
Mixed ores . . .	7,916	3,770	11,686
Pyritic lead-ore . .	805	64	869
Copper-matte . .	6,288	...	6,288
Lead-matte . . .	3,377	...	3,377
"Spurstein" (regulus).		1 620	1,620
Total . . .	25,103	6,510	31,613

Composition of these materials:—

	Copper ore.			Mixed ore	Pyritic lead-ore	Copper-matte	Lead-matte	Regulus
	1.	2.	3.					
Cu .	17·70	9·70	4·75	4·60	1·05	30·47	18·20	64·38
Fe .	23 00	30·40	33·50	12·40	24·50	24·40	21·70	8·93
Zn .	9·50	5·80	4·90	21·50	15·50	8·75	15·00	1·34
Pb .	3·70	2·40	1·75	10·05	6·75	5·80	7·10	2·95
S .	32·00	36·00	40·50	24·00	34·00	18·70	17·00	20·70

The production of acid at Oker is per annum 21,000 tons 50° B., in five sets of chambers of 19,656 cbm. capacity, *i.e.*, 1068·38 kg. acid of 5° B., per 1 cbm. chamber-space. The kiln-gases contain 4 to 5 per cent. SO_2.

Traces of Hg, Tl, Cd, and Se have been found both in the ores and in the products obtained therefrom.

Apart from pure pyrites, the "ordinary ores" are best adapted for vitriol-making, because they contain their sulphur mostly as FeS_2; the "mixed ores" are less favourable, on account of their galena, and the rich copper-ores on account of their large percentage of copper. Of the lead-ores only those amply permeated by pyrites are fit for vitriol-making. The sulphur in the ores worked at Oker varies from 20 to 40 per cent.; on an average it is 30 per cent.; but it must be noticed that the sulphur of the galena is altogether unavailable for vitriol-making. The case is not much better when copper-pyrites predominates, because this furnishes too poor a gas, and, moreover, decrepitates and falls to powder in roasting. If no more than 35 per cent. of copper-pyrites is mixed with iron-pyrites, it does no harm. Blende behaves in a similar way, but rather more favourably; ores containing 35 per cent. blende along with 25 per cent. pyrites yield gas quite adapted for vitriol-making.

The first sulphuric-acid works at Oker were erected in 1841; there is now one of the largest acid works in Germany, viz., 14 sets of chambers with a capacity of 800,000 cub. ft.

In the *Eng. and Min. J.*, 1904, lxxviii., p 216, there is a report on the utilisation of the sulphur contained in the Broken Hill ore, as treated by the Carmichael-Bradford process. The raw material is mixed with 15 to 25 per cent. gypsum, the mixture is broken up to the size of marbles and roasted in converters in such manner that the temperature in the lower part reaches 400° to 500°. When air is passed through it, SO_2 is given off, partly also from the gypsum, and the gases are passed into lead chambers, where about 350 kg. of sulphuric acid is recovered from 1 ton of ore, containing 14 per cent. sulphur. The plant at that time yielded 35 tons chamber acid per week, and it was to be enlarged.

"*Coarse metal*" of copper-smelting is roasted for the manufacture of sulphuric acid at Mansfield. A product containing 34 per cent. Cu, 28 per cent. Fe, and 28 per cent. S, according to Bode, yields gas with 5½ per cent. by volume of SO_2, and at a sufficiently high temperature to work with the Glover tower. In most cases, up to the present, coarse metal cannot be roasted so as to utilise the SO_2.

Galena was formerly nowhere worked in such a way as to extract its sulphur in the shape of sulphuric acid. The purest galena contains only 13·4 per cent. of sulphur; it is transformed into lead sulphate on roasting, and only in the strongest white heat gives off a portion of its sulphur as SO_2; moreover the metallurgical processes to which it is subject are of such a nature that only poor gas can be produced from it. This subject has been discussed by Bode in his *Beitrage zur Theorie und Praxis der Schwefelsaure-fabrikation*, 1872, pp. 32 and 63; his conclusion is that even mixtures of galena and pyrites cannot be roasted in kilns for the manufacture of sulphuric acid if they contain more than 18 to 20 per cent. of galena. Quite recently, as I learn from a private source, the SO_2 from galena is obtained in a sufficiently concentrated form for utilisation, by blowing the galena with air in Bessemer converters.

Lead-matte is used for the manufacture of sulphuric acid—for instance, at Freiberg and in the Lower Harz; it is there roasted in large kilns of 12½ tons capacity. The matte loses half its sulphur, and yields gas with 4 to 6 per cent. of SO_2; the temperature, according to Bode, is high enough for the Glover tower. In the Upper Harz the utilisation of its sulphur in metallurgy has in general not been found practicable.

5. By-products of other Manufacturers.

Spent Oxide from Gas-works.

We have already (*suprà*, p. 36) treated of this oxide as a material for obtaining free sulphur. We shall now describe it in respect of its application for the manufacture of sulphuric acid, which is carried on in many places.

Coal-gas is universally purified from sulphuretted hydrogen by passing it over hydrated ferric oxide. The H_2S of coal-gas is due to the presence of pyrites, contained in the coal, the S of which appears in the gas mostly as sulphuretted hydrogen. Most works remove this from the gas by a mixture of hydrated iron oxide and sawdust. In this case sulphide of iron and sulphur are formed, according to the equation

$$2Fe(OH)_3 + 3H_2S = 2FeS + S + 6H_2O;$$

and when the mass, having become inactive, is exposed to the air, it again passes over into ferric hydroxide, more sulphur being precipitated, thus:

$$2FeS + O_3 + 3H_2O = 2Fe(OH)_3 + S_2.$$

The hydroxide thus reproduced and mixed with sulphur is again used in the purifiers, and is regenerated about thirty or forty times over before the sulphur has accumulated therein to such an extent that the mixture does not work any longer; it is then replaced by fresh oxide, and the spent ore is passed over to vitriol-makers.

Phipson states the composition of such a mass to be:—

Water	14 per cent.
Sulphur	60 „
Organic substance insoluble in alcohol	3 „
Organic substance soluble in alcohol (calcium ferrocyanide and sulphocyanide, ammonium sulphocyanide, ammonium chloride, hydrocarbons)	1·5 „
Clay and sand	8 „
Calcium carbonate, ferric oxide, etc.	13·5 „

If the oxide contains considerable quantities of cyanides, it may cause great trouble in the manufacture of sulphuric acid (31*st Alkali Report*, p 89).

Hot water extracts the ferrocyanides and sulphocyanides, together with ammonium chloride; the solution can be evaporated to dryness, and the residue separated by alcohol into insoluble calcium ferrocyanide and soluble sulphocyanide and chloride.

According to the analyses of Davis (*Chem News*, 1874, xxix. p 30), three samples of spent oxides contained:—

	I	II	III
Sulphur	64·376	62·358	67·956
Ferric hydroxide	14·121	17·112	15·335
Insoluble	11·052	5·099	8·304
Moisture	2·079	5·387	3·900
Lime (as CaS)	2·699	..	...
Sawdust	2·470	1·776	1·002
Calcium carbonate		5·135	3·006
Ammonium sulphocyanide	2·662	1·324	1·102
Ammonium chloride	0 605		
Ammonium cyanide		...	
Ammonium ferrocyanide	...	1·663	..
Prussian blue	trace	0·366	trace
Total	100·064	100·220	100·105

These samples seem to have been taken from precipitated iron hydroxide, to judge from further analyses by Davis (*Chem. News*, xxxvi. p. 189), in which also tarry substances are taken into account.

The following table gives the composition of waste gas-oxide, proceeding from different raw materials:—

	Precipitated $Fe(OH)_3$	Bog-iron-ore.	Copperas	Bad oxides
Ferric hydroxide	17·74 to 19·36	15·96 to 26·42	5·01 to 6·84	8·72 to 20·40
Sawdust . .	1·98 ,, 4·72	1·14 ,, 3·72	1·04 ,, 3·24	2·16 ,, 9·76
Calcium carbonate	0· ,, 1·04	0· ,, 1·73	0·	0· ,, 10·36
Ammonium sulphocyanide .	1·99 ,, 2·74	0·94 ,, 1·93	1·98 ,, 3·41	1·18 ,, 4·72
Ammonium ferrocyanide . .	trace	trace ,, 0·21	0·27 ,, 0·64	trace ,, 0·44
Tarry matters .	0·72 to 1·22	0·92 ,, 1·14	0·72 ,, 1·18	0·55 ,, 1·04
Sulphur . .	62·44 ,, 67·18	48·76 ,, 57·44	18·76 ,, 55·74	32·42 ,, 42·16
Insoluble in dilute HCl . .	3·66 ,, 5·47	9·74 ,, 11·42	7·82 ,, 12·68	12·12 ,, 20·71
Prussian blue .		trace ,, 0·17	trace ,, 1·71	trace ,, 2·64
Calcium sulphate			trace ,, 1·43	0· ,, 3·23
Ammonium sulphate . .	...	...	12·78 ,, 16·72	0· ,, 1·14
Moisture (by diff.)	4·72 ,, 5·76	7·22 ,, 10·82	7·98 ,, 9·22	7·49 ,, 33·41

From these analyses it can be seen, first, that it is decidedly best to extract the mass at first with water, in order to remove the ammonia compounds, which are in themselves valuable, and which, if they get into the chambers, destroy a good deal of nitre (their value is certainly greatly lessened by the sulphocyanide); secondly, that sometimes a considerable quantity of calcium carbonate is present, which may get into it at the gas-works by lime being added, on purpose or by mistake, and which, of course, retains an equivalent quantity of sulphur in the shape of gypsum. In fact a sample of the residue left after burning contained:

Insoluble . .	33·386	Calcium sulphate .	13·315
Ferric oxide .	52·399	Sulphur . .	0·200

These impurities (which cause a loss by retaining sulphuric acid) and the sulphates present from the first (which are not available) must be allowed for in *analysing* the gas oxide. This, according to Davis, was formerly done by extracting the sulphur by means of carbon disulphide, evaporating the solution, and weighing the sulphur; but as the presence of tarry matters causes an error, Davis now makes the analysis by burning the sulphur in a current of air in a combustion-tube of Bohemian glass, conducting the SO_2 formed into an absorbing-apparatus filled with iodine solution, and retitrating the unaffected iodine by a solution of sodium thiosulphate (*Chem. News*, xxxvi. p. 190; *cf.* also Zulkowsky's process, p. 72).

Pfeiffer (*J. Gasbeleucht.*, 1905, p. 977) estimates the S in spent gas-oxide by burning 1 g. in a bottle filled with oxygen, containing 25 to 50 cm. normal NaOH solution. If the sample should not take fire, it is taken out, glycerin is poured over it, a priming-match is put in, which is lighted and the sample put back into the bottle. When the combustion is completed, 1 c.c. of neutral hydrogen peroxide is put in, and the NaOH in excess titrated with acid and methylorange.

The *burning* of gas-oxide is usually performed in shelf-furnaces similar to those used for pyrites-smalls. They will be described in detail in Chapter IV. Already in 1861, at Barking Creek, on the Thames, 2180 tons of this material were used; but much larger quantities might have been got, since, according to A. W. Hofmann (*Report*, 1862, p. 15), even at that time at least 10,000 tons of sulphur were contained in the London gas. Much of the acid made from spent oxide is sold as "brimstone acid."

In France also, at that time, the sulphur from gas-works was used on a large scale for the manufacture of sulphuric acid. The factory at Aubervilliers, belonging to the Society of St Gobain, used no other; Messrs Seybel & Co. at Liesing, near Vienna, and Kunheim & Co. at Berlin (Wagner's *Jahresber.*, 1864, p. 153; Hasenclever, *loc. cit.*, p. 167) did the same.

The rational treatment of spent oxides for the purpose of obtaining ammonium salts, ferrocyanides, and sulphocyanides is described in Lunge's *Coal-tar and Ammonia*, 4th edition (1909), pp. 887 and 1128.

According to the 41*st Alkali Report*, p. 105, the manufacture of sulphuric acid from spent oxide requires very close watching, on account of the variation in the nitrate-consuming compounds which it contains. Certain kinds of spent oxide cannot be burnt without seriously disorganising the chamber-process, unless the oxide is first washed.

Sulphuretted Hydrogen.

The sulphur contained in Leblanc *alkali-waste*, in the shape of calcium sulphide, has been frequently proposed for the manufacture of sulphuric acid, nearly always after having first converted it into *sulphuretted hydrogen*. The only successful process in this line (the Chance process of treating alkali-waste) belongs to the domain of alkali-manufacture, and cannot be treated in this volume; it is described in our third edition, Vol. II., pp. 945 *et seq.* (1909). Only the contrivances for *burning* the hydrogen sulphide will be described in Chapter IV.

Borntrager (Ger. P. 15757) proposes decomposing the yellow liquors from alkali-waste by means of ferric oxide (ground damp pyrites cinders), to filter the sulphur and ferric sulphide which is thus precipitated, and burn it after drying in ordinary shelf-burners. [Oxide of iron in this state is a very inferior reagent for removing the sulphur from yellow liquors and the like.]

An anonymous inventor has proposed to absorb the sulphuretted hydrogen in hydrated ferric oxide suspended in water, filter, press the residue, dry it, and burn it on shelf-burners. Wyss (*Bull. Soc. Ind. Mulhouse*, 1890, p. 281) has shown that this process is neither novel nor in any way promising of success.

The sulphuretted hydrogen given off in the manufacture of sulphate of ammonia (cf. Lunge's *Coal-Tar and Ammonia*, 4th edition, pp. 1085 *et seq.*) is sometimes used for the manufacture of sulphuric acid. Here the H_2S is not merely diluted with a large quantity of inert gases, but is also of very unequal concentration, which formerly rendered the manufacture of sulphuric acid from this source an unprofitable process. The same must be said of most other cases in which H_2S is given off as a by-product.

The utilisation of the H_2S from sulphate-of-ammonia works for the manufacture of sulphuric acid has, however, been greatly improved and is now no longer a rare exception, but is practised in a good many English works. If the gas is properly introduced into the burner (*cf.* Chapter IV.), the consumption of nitre is not excessive, and it is even possible to increase the heat by this means, if the spent oxides should not suffice for this purpose. The action of the large quantity of carbon dioxide accompanying the H_2S in the case of sulphate-of-ammonia works would seem to consist only in requiring a certain amount of chamber-space, contrary to the opinion reported in Chapter VIII.

The H_2S given off in the refining of asphaltum at Ventura (Colorado) is burnt and 10 tons of high-grade sulphuric acid daily are made therefrom (*Iron Age*, 10th July 1902).

Feld (Ger. P. appl. F26516) takes H_2S and SO_2 out of gases and vapours by allowing them to act on solutions or suspensions of compounds of zinc, manganese, or iron, if necessary together with ammonia, and with air or other oxidising agents, with or without heating, so as to obtain sulphur, or sulphuric acid, or sulphates.

F. Perry (B. P. 20063, of 1911) utilizes the H_2S contained in producer-gas, etc., by allowing the gas to act upon a solution of cupric sulphate, whereby sulphuric acid is set free and cuprous sulphide is precipitated. The latter is roasted, whereby 70 per cent of it is converted into sulphate, the remainder into oxide.

Sulphur Dioxide from other Sources.

Sulphur dioxide, formed in many manufacturing operations as a disagreeable by-product, apart from those already described (*suprà*, pp. 112 *et seq.*), is sometimes proposed to be converted directly or indirectly into sulphuric acid. The special cases in which this has been attempted will be treated in the next chapter.

6. NITRATE OF SODA.

Commonly called "Nitre." Its composition is: $NaNO_3$.

$\frac{1}{2}(Na_2O)$ -	31·00	36·49 per cent.
$\frac{1}{2}(N_2O_5)$ -	54·01	63·51 ,,
	85·01	100·00

Hardness 1·5 to 2; sp. gr. 2·09 to 2·39. In the pure state, and in large crystals, it is colourless, transparent, and brilliant as glass; in small crystals it is white and opaque. The crystals are rhombohedra with angles of 106° 30′ and 73° 30′. It has a cooling, bitter taste. Heated to a certain temperature it melts; at a red-heat it is decomposed into sodium nitrite and oxygen gas. The fusing-point is 316° to 319° C. (Carnelley, *J. Chem. Soc.*, 1878, ii. p. 277). Mixed with coal, it deflagrates on heating. It attracts moisture from the air (especially if not quite free from chlorides), and readily dissolves in water, with considerable lowering of the temperature.

One part of sodium nitrate, according to Marx, requires for solution 1·58 part of water at −6°, 1·35 at 0°, 0·46 at +119° C. According to Kopp, 1 part of sodium nitrate at 18°·5 C. requires 1·14 of water, or 100 parts of water dissolve 87·72 parts of the salt. In the presence of sodium chloride, its solubility is considerably less.

Specific Gravity of the Solutions of Sodium Nitrate at 20° C.

Parts of salt in 100 water	Specific gravity	Parts of salt in 100 water	Specific gravity	Parts of salt in 100 water	Specific gravity.
1	1·0065	18	1·1260	35	1·2679
2	1·0131	19	1·1338	36	1·2770
3	1·0197	20	1·1418	37	1·2863
4	1·0264	21	1·1498	38	1·2958
5	1·0332	22	1·1578	39	1·3055
6	1·0399	23	1·1659	40	1·3155
7	1·0468	24	1·1740	41	1·3255
8	1·0537	25	1·1822	42	1·3355
9	1·0606	26	1·1904	43	1·3456
10	1·0676	27	1·1987	44	1·3557
11	1·0746	28	1·2070	45	1·3659
12	1·0817	29	1·2154	46	1·3761
13	1·0889	30	1·2239	47	1·3864
14	1·0962	31	1·2325	48	1·3968
15	1·1035	32	1·2412	49	1·4074
16	1·1109	33	1·2500	50	1·4180
17	1·1184	34	1·2589		

Nitrate of soda occurs in many places in small quantities; but the only large beds which supply the world with this article are situated in a region of the west coast of South America, formerly belonging to Peru and now to Chili. This occurrence, and the industry founded thereon, have been described in various communications by Langbein (Wagner's *Jahresber.*, 1871, p. 300; 1872, p. 290; 1879, p. 390); also by W. E. Billinghurst, of whose book (written in Spanish) Darapsky gives an extract in the *Chem. Zeit.*, xi. p. 752 (*J. Soc. Chem. Ind.*, 1887, p. 545). *Cf.* also Buchanan (*ibid.* 1893, p. 128) and Behrend (*Z. deutsch. Ingen.*, 1899, p. 1199; *Fischer's Jahresber.*, 1899, p. 406). A special booklet on the Chilian nitrate industry has been published by Semper and Michels, Berlin, 1904. A very complete report on this industry was made by the German Consulate in Antofagasta, *Chem. Ind.*, 1911, pp. 758-761.

The nitre-beds are principally situated in the province of Tarapacá, between 68° 15′ and 78° 18′ longitude, and 19° 12′ and 21° 18′ 30″ latitude; they also occur somewhat south, especially near Antofagasta and Taltal. They were discovered in 1821 by Mariano de Rivero, and have been worked since 1830. The nitre zone is situated at an altitude of 3600 ft. above the sea-level.

In 1863 Don José Santos Ossa discovered the nitre-beds, called Salar del Carmen, between the 24th and 22nd degree of latitude, and the beds of Aguas Blancas, south-west of Antofagasta (23rd degree of latitude), both situated in the province of Antofagasta, at that time belonging to Bolivia, now to Chili. A Chilian Limited Company was founded for working them, first that of Salar del Carmen, and started work in 1869, at first in a very primitive way by lixiviating the caliche in open-fired pans. In 1871 machines were introduced, and the production rose to 15,000 quintals per month; a narrow-gauged railway was also built from Antofagasta to Salar, and in 1875 continued to Carmen also; the production of those fields now got up to 100,000 quintals per month, and was expected to rise to 120,000 quintals (6000 tons) per month in 1895. The railways leading to these fields were sold to the English Antofagasta & Bolivia Railway Co., comprising 574 miles. More recently several other nitre-beds, situated near that railway line, have been started: (1) An Italian Company, the Oficina Lastenia, near Salinas station (exporting 52,000 tons per annum); (2) an English Company, Oficina Anita (exporting 75,000 tons per annum); (3) another English Company, Oficina Lucie (exporting 75,000 tons), all of them with modern German machinery, working by electricity; (4) Oficina Riviera (40,000 tons); (5) Oficina Ausonia, and (6) Oficina Filomena, all of them owned by Italians; and several new oficinas were to be erected. The working of the Aguas Blancas fields, 61 miles by rail from Antofagasta, commenced only in 1881, and was stopped a few years after, the expense of carriage to the coast being too great. Only in 1892 the mines were again started by a Spanish firm. A number of oficinas was then erected by this and by a German firm. The whole production of the Antofagasta district in 1905 was 543,000 tons per annum, and was expected to be considerably increased, so that it is now an important rival to the earlier worked Tarapacá district.

An enquiry made by the Chilian Government (*Z. angew. Chem.*, 1907, p. 592) on the extent of the nitre area showed that the State possessed 2,000,000 hectares of it (say 5,000,000 acres), containing at least 1,000,000,000 tons of nitrate, which would cover the highest demands for exportation for about one hundred and twenty-five years; apart from the three- or four-fold larger nitre-bearing area, now in the hands of private persons and companies.

A detailed report on the situation of the Chilian nitrate industry has been made by Hartwig in *Chem. Zeit.*, 1909, p. 1162. Since 1908, when the nitrate trust broke down, the production of nitre has grown apace. Moreover, the constantly increasing production of synthetic nitrates influences the market to such an extent that, *e.g.*, Denmark since 1908 has bought no more nitrate from Chili; Sweden will soon follow, and East India, Africa, and Peru consume essentially less, while other countries consume more. The prices have also considerably receded. Evidently in future the older, well-established factories will supply the market in free competition, but the others must either cease to work or pass into the hands of their more powerful competitors. Similar opinions are found in the report of the German Consulate at Valparaiso in *Z. angew. Chem.*, 1910, p. 1465; in *Chem. Ind.*, 1910, pp. 400 and 588. The producing-cost of nitrate up to the place of shipment, without interest and amortisation, ranges from $4 to $17 and averages $12; to this comes $11 export duty. The total stock of nitrate in the north of Chili is estimated at 245,827,000 tons, which would cover the present consumption for the next fifty years.

Further reports on the Chilian nitre industry have been made by the United States Consul (*J. Ind. Eng. Chem.*, 1909, pp. 45-47) and by the German Consul in Antofagasta (*Chem. Ind.*, 1911, p. 760). In the year 1910 there were in Chili 155 nitre-factories ("oficinas"), of which only 100 were actually at work—65 factories belonging to English, 53 to Chilian, 15 to German firms.

The nitre-bearing rock, called *caliche*, is found in layers of from 10 in. to 5 ft. in depth, which rarely crop out at the surface. The overlying rock, called *costra*, is 18 in. to 7 ft. thick, and consists principally of a hard conglomerate of sand, felspar, phosphates, and other minerals.

The composition of the caliche varies; it contains from 48 to 75 per cent. of sodium nitrate, 20 to 43 per cent. of sodium chloride, and varying quantities of sodium sulphate, calcium sulphate, potassium nitrate, potassium iodate, magnesium chloride, insoluble earthy portions and organic substance (guano). It is first broken by a stone-breaking machine, and then put into the dissolvers. These are partly open square tanks, preferably, however, closed egg-shaped boilers with two manholes—one on the top for filling in the caliche, another at the bottom for emptying the residue. The mass rests on a perforated bottom. The boilers are filled entirely with the broken rock, and half with mother liquor, and were formerly always heated by direct steam injected below the false bottom. After one and a quarter to two and a half hours the liquid, then sufficiently saturated with nitre, is run into settlers; from these it flows, after several hours, into a second settler, where, by half an hour's rest, it allows some still-suspended common salt to subside, and then runs into shallow coolers. The residue from the dissolvers, which still contains 15 to 35 per cent. of sodium nitrate, is either emptied at once or boiled again with fresh water. The crystals, separated in the coolers after draining off the mother liquors, are spread in layers of 12 to 18 in. thickness on a large surface exposed to draught, and dried with frequent stirring. The total cost of sodium nitrate, up to its reaching European ports, in 1871, amounted to £8, 18s. per ton, which left a good margin for profit at the average price of £12 (it has reached £16 and more). At present both the producing and selling prices are much lower.

The above-described system of dissolving by open steam was afterwards abandoned for closed steam-coils or similarly-acting apparatus; at the same time air heated to 120° to 150° C. is forced through the liquid by means of injectors, in order to hasten the evaporation. This produces both stronger and purer liquors, the quantity of sodium chloride being the same in the stronger as in the weaker liquor.

Fairweather (as communicated from Beaver and Nordenflycht, B. P. 7478 of 1906) describes an improved arrangement of the dissolvers for caliche.

The composition of the crude nitre-earth is shown by the following analyses (see Table, p. 127).

The analyses *a* and *b* (*a* white, *b* brown caliche) are by Machattie (*Chem. News*, xxxi. p. 263). They are somewhat suspicious, both on account of the total absence of potassium salts and of the extremely improbably high percentage of sodium iodate. This is all the more noticeable as Machattie at the same time states the average percentage of iodine in five samples of *mother liquor* to be $=0{\cdot}56$, equal to 0·873 per cent. of sodium iodate, which may be nearer the truth. The analyses *c*, *d*, and *e* are by V. L'Olivier (*Comptes rend.*, 26th October 1875). The analyses of caliche by Dafert in *Monatsh.*, 1908, pp. 235 *et seq.*, show nothing new in that respect.

	Caliche.				Costra
	a.	*b.*	*c.*	*d.*	*e.*
Sodium nitrate	70·62	60·97	51·50	49·05	18·60
Sodium iodate	1·90	0·73	..	...	...
Sodium iodide	...	...	traces	traces	..
Sodium chloride	22·39	16·85	22·08	29·95	38·80
Sodium sulphate	1·80	4·56	8·99	9·02	16·64
Potassium chloride		...	8·55	4·57	2·44
Magnesium chloride		...	0·43	1·25	1·62
Magnesium sulphate	0·51	5·88	...		...
Calcium sulphate	0·87	1·31			...
Calcium carbonate	...	..	0·12	0·15	0·09
Silica and ferric oxide	...		0·90	2·80	3·00
Insoluble	0·92	4·06	6·00	3·18	20·10
Moisture	0·99	5·64	...	..	...
Total	100·00	100·00		...	..

The *iodine* contained in the mother liquors is now recovered to a great extent, and forms one of the principal sources of this article.

Graeff (*Eng. and Min. J.*, 1910, p. 173) describes the nitre-beds of the California Nitrate Co. in the East of San Bernardino County (South California), occupying over 12,000 acres; he gives an analysis of samples from that locality, showing from 7·2 to 22·6 per cent. $NaNO_3$ Owing to the abundance of water, this deposit would be more easily worked than the Chilian fields.

A rich deposit has been discovered in the Mohave Desert, of which, according to *Eng. and Min. J.*, 1903, p. 186, about 21,000,000 tons are visible; but "this figure is likely to be revised." Reports on rich beds of nitre in the Colorado River district have been shown to be grossly exaggerated by Turner (*Z. angew. Chem.*, 1907, p. 1157).

Another bed of nitrate of soda has been found in the South-

American State of Colombia (*J. Soc. Chem. Ind.*, 1894, p. 1001). It is about 100 km. distant from San Juan de la Cienaga, and had been proved up to that time for a surface of 75 sq. km. It has a thickness of from 30 cm. to 3 m., and averages 11 to 12 per cent. $NaNO_3$, together with calcium carbonate, calcium sulphate, and silicates. The recoverable nitre is estimated to exceed 7,000,000 tons, but none of it is as yet in the trade. Another bed has been discovered in Texas; this is stated to contain 98 per cent. pure nitrate (*Chem. Ind*, 1902, p. 265).

A deposit of *potassium nitrate* has been found near Cochabamba, in Bolivia (Sacc, *Comptes rend.*, xcix. p. 84). This deposit, reported to be enormous, but not yet worked, consists of 60·70 per cent. potassium nitrate, 30·70 borax, a little salt and water, 8·60 organic substances. On dissolving the saline mixture in hot water and cooling, pure potassium nitrate crystallises out.

The exportation of nitrate of soda from Chili during recent years has been as follows:—

	1898.	1899	1900.	1901.	1902.
	Tons	Tons.	Tons.	Tons	Tons.
Continent of Europe	904,500	981,000	1,026,000	1,036,000	897,000
United Kingdom	132,500	121,000	126,000	118,000	111,000
United States	125,000	133,000	170,000	192,000	185,000
Other countries	16,000	25,000	28,000	18,000	16,000
Total	1,178,000	1,260,000	1,350,000	1,364,000	1,209,000
Price on 31st Dec., per cwt.	...	7s. 9d.	8s. 6d.	9s.	...

	1906	1907.	1908.	1909.	1910.
	Tons	Tons	Tons.	Tons.	Tons.
Production	1,800,819	1,816,917	2,087,564	2,239,723	2,625,000
Consumption in Europe	1,335,689	1,247,540	1,644.505	1,583,278	1,651,000
,, in United States	330,805	341,470	326,818	453,831	510,000
,, in other countries	40,904	27,175	55,367	70,401	89,000
Total consumption	1,702.399	1,636,187	2,026,690	2,101,510	2,250,000

In 1903 the American statistician, Vergara, estimated that if the consumption of nitrate of soda went on increasing at the same rate as hitherto, the Chilian beds would be completely exhausted in 1923.

Bernthsen (*Z. angew. Chem.*, 1909, p. 1169) states the exportation of nitre from Chili in 1908 = 1,730,000 tons, of which Germany consumed 450,000 for agricultural purposes and 150,000 in its chemical industries.

Exports and Imports of Nitrate of Soda from and into the United Kingdom (from the Blue book for 1910).

	1906.	1907.	1908.	1909.	1910.
Imports . tons	108,486	113,894	145,724	90,207	126,498
Exports . ,,	4,723	6,529	10,662	6,917	7,133

Germany in 1910 imported from Norway 780 tons nitrate of soda (against 825,000 tons she got from Chili) and 11,368 tons nitrate of lime.

Statistics of previous years are given in the former editions of this book.

When *emptying nitrate of soda from the bags* a certain quantity of the salt, which is always damp, remains adhering to them; this not only causes loss, but renders them useless, and even produces a danger of fire. It is therefore well to lixiviate the bags with hot water and to dry them. The solution is evaporated to a small bulk and crystallised. The mother liquor from this operation is always very rich in chlorides, which seems to show that the deliquescence of sodium nitrate is not a property of the pure salt, but is owing to the magnesium and calcium chloride contained in it, since the dampest salt will adhere to the bags. The washed and dried bags should not be stored in quantity, as they are still very inflammable.

Composition of Commercial Nitrate of Soda.—R. Wagner (*Jahresber.*, 1869, p. 248) found in commercial nitrate of soda:—

Sodium nitrate	94·03
,, nitrite	0·31
,, chloride	1·52
Potassium chloride	0·64
Sodium sulphate	0·92
,, iodate	0·29
Magnesium chloride	0·93
Boric acid . . .	traces
Moisture . . .	1·36
	100·00

The nitrate of soda imported into England, as used by vitriol-makers, is much purer than the above sample. The English sellers mostly guarantee a maximum of 5 per cent. "refraction" (that is, the total percentage of all foreign constituents, inclusive of water), frequently, however, 4 or even 3½ per cent. refraction. English vitriol-makers would, indeed, altogether refuse nitrate containing upwards of 3 per cent. of chlorides, like that analysed by Wagner, 1 per cent. being the maximum allowed. The hydrochloric acid generated from them, of course, gives, with nitric acid, free chlorine and its compounds with nitrogen oxides, and causes a loss of the latter. The average composition of nitrate for chemical works is—

96 sodium nitrate (including nitrate, iodate, etc.),
0·5 chlorides (calculated as NaCl),
0·75 sulphates (calculated as $NaSO_4$),
2·75 moisture.

Gilbert (*Z. angew. Chem.*, 1893, p. 495) pointed out that the Chilian nitre always contains, and always has contained, some *potassium nitrate.* He states that the percentage of KNO_3 rarely exceeds 5 per cent., and the deficiency of nitrogen caused thereby is more than compensated by the value of the potassium for agricultural purposes. The old method of testing for "refraction" is obstinately adhered to by the producers, and is preferred by Gilbert to the direct guarantee of 15·57 per cent. nitrogen demanded by the agricultural control-stations. Jones (*loc. cit.*, p. 698) mentions that he had met with nitre containing much more potash; but this nitre, which is recovered from the bilge-water of the carrying vessels, occurs only quite exceptionally (*cf.* below). Most sulphuric-acid manufacturers do not share Gilbert's opinion: see below.

An impurity formerly entirely overlooked in commercial nitrate of soda consists in *perchlorate* and *chlorate* of sodium. Beckurts (*Arch. Pharm.*, ccxxiv. p. 323) found in all descriptions of commercial nitre small quantities of chlorates and perchlorates, and this has been confirmed from all sides. A large number of methods have been devised for estimating the perchlorate (*cf.* Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i. pp. 319 *et seq.*), all of which are practically founded upon converting the perchlorate into chloride, preferably by fusing the nitrate with lime or sodium carbonate and manganese peroxide, estimating the chloride in the ordinary way, and deducting the chloride previously existing in the nitrate.

In order to manufacture nitrate of soda free from perchlorate, which does not occur in the first crystallisation, but accumulates in the mother liquors, and after using these three or four times over contaminates the nitrate crystals up to 1 per cent., Foelsch & Co. (Ger. P. 125206), cools down the impure mother liquors to 0° C., 1 cbm. of which then furnishes 160 kg. of a mixture of salts, containing 150 $NaNO_3$ and $NaClO_3$. The new mother liquor, when employed for redissolving crude nitre, at first furnishes nitrate free from perchlorate.

Egor (Ger. P. 165310) for the same purpose treats the crude nitrate with just enough cold water to dissolve all the $NaNO_3$, but to leave all potassium nitrate and perchlorate behind.

Analysis of Nitrate of Soda.

In the laboratories working for the importers of nitrate of soda the value of nitrate is mostly only estimated indirectly, viz., the "refraction." Ten g. are well dried in a porcelain capsule, weighed again, dissolved, the residue (if any) is estimated, the liquid dissolved to a certain volume, and in separate portions of the liquid the chloride and sulphate are estimated in the usual way. The sum total of moisture, insoluble residue, sodium chloride, and sodium sulphate is called the "refraction," and it is assumed that the remainder is real sodium nitrate (*cf.* p. 130). This may, however, lead to very erroneous results, where, for instance, the nitre contains some potassium nitrate. A case in point has been described by me in *Chem. Ind.*, 1883, p. 369, where an error amounting to 2 per cent. was caused in this way. Perchlorate causes also errors; and altogether it stands to reason that the consumer of nitrate receives justice only by a real determination of the nitric acid contained in (or, more properly speaking, to be evolved from) a sample of nitrate. On the other hand, the interests of the importers and dealers in nitrate are quite in the opposite direction. According to *Fischer's Jahresber.*, 1899, p. 407, the Hamburg importers insist upon the "indirect" (*i.e.*, altogether deceptive) analysis, and want the perchlorate to be counted as nitrate.

The direct analysis, *i.e.*, the estimation of the $NaNO_3$ (or its equivalent of KNO_3), can be carried out in many ways, a complete enumeration of which is found in Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i. pp. 309 *et seq.* Among these, those mostly used are the Schloesing-Grandeau and the Ulsch methods (*cf.* below, in the section on Nitric Acid), but at sulphuric-acid works the method nearly always employed is Lunge's "*nitrometer method*," which is carried out as follows:[1]—

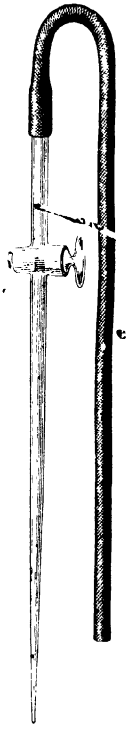

FIG. 9.

Dissolve a good-sized sample, say 20 to 30 g., of the nitrate in twice its weight of water, employing a flask of known contents and heating very gently. Weigh out a quantity corresponding to about 0·4 g. $NaNO_3$ in an ordinary weighing-glass or in a tube with stopcock, as employed for testing fuming sulphuric acid (Fig. 9). Run its contents into a nitrometer, either a "bulb-nitrometer," as shown in Fig. 10, or, preferably, the non-graduated agitating-vessel connected with a Lunge's gas-volumeter, to be described in the next chapter. In the latter case no observation of temperature and barometric pressure nor any reduction tables are required. Do not rinse the weighing-tube (which would dilute the liquid too much), but weigh it back as it is. Decompose the solution within the nitrometer with a sufficient quantity of strong sulphuric acid and mercury, and measure the nitric oxide given off as will be described in the next chapter, where also a table for reducing the readings to $NaNO_3$ will be given.

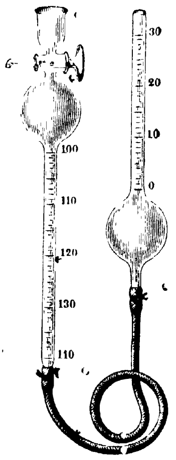

FIG. 10.

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[1] The nitrometer in its use for the analysis of nitrous vitriol will be described in Chapter III.

7. NITRIC ACID, NO_3H.[1]

This may be called one of the raw materials of vitriol-making, although a manufactured product itself, in those works which employ it in lieu of solid nitrate of soda.

Nitric acid proper (the monohydrate) has the equivalent 63·02 (O = 16), and may be said to contain, as formerly expressed, 85·71 nitric anhydride (N_2O_5) and 14·29 water. Its sp. gr. is 1·54 at 20°, or 1·55 at 15°. It is colourless if perfectly pure; but the strongest acid of commerce is always coloured yellow, or even red, by a partial decomposition into oxygen and nitrogen peroxide, N_2O_4 (hyponitric acid). Its boiling-point is 86° C. On boiling an acid containing a little water, at first strong acid distils over, till the boiling-point of the remainder has reached 126°, at which point the thermometer remains stationary, and an acid of constant composition for any certain pressure distils over. Exactly the same point is reached from the opposite side by distilling more dilute acids, in which case water distils over, and the remaining acid becomes more and more concentrated, till the above stationary point is reached. The acid at that point has nearly the composition $2NO_3H + 3H_2O$ (corresponding to 60 N_2O_5 and 40 H_2O) and a sp. gr. of 1·42.

Erdmann (*Z. anorg. Chem.*, xxxii. p. 431) asserts having isolated several hydrates of nitric acid in a crystallised state, but Kuster and Kremann (*ibid.*, xli. pp. 1-42) strongly contradict his statements. That question has no technical interest, wherefore we abstain from going into it.

The following table shows the boiling-points of nitric acid of various strengths:—

Specific gravity.	Boiling-point.	Specific gravity	Boiling-point
	Degrees C.		Degrees C.
1·15	104	1·42	123
1·20	108	1·48	115
1·30	113	1·50	99
1·35	117	1·52	86
1·40	119		

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[1] Some interesting notes on the early history of manufacturing nitric acid in England are contained in Guttmann's paper, *J. Soc. Chem. Ind.*, 1901, p. 7. The cost of producing 200 lb. of acid sp. gr. 1·375 in 1771 was £8, 2s. 2d. without labour. See also W. P. Reid's notes, *ibid.*, p. 8.

For the percentage of nitric acid for different specific gravities, Kolb (*Bull. Soc. Ind. Mulhouse*, 1886, p. 412) has given a table which is now rendered obsolete by the more accurate table given below, which is derived from the experiments of Lunge and Rey (*Z. angew. Chem.*, 1891, p. 165). The specific gravities are taken at 15° C., referred to water of 4° and reduced to the vacuum. They refer to *chemically pure* nitric acid; commercial acid, containing nitrous acid, etc., contains less real HNO_3 at the same specific gravity.

Specific Gravities at $\frac{15^\circ}{4}$.	Degrees Twad.	100 parts by weight contain		1 litre contains kg.	
		N_2O_5.	HNO_3.	N_2O_5	HNO_3.
1·000	0	0·08	0·10	0·001	0·001
1·005	1	0·85	1·00	0·008	0·010
1·010	2	1·62	1·90	0·016	0·019
1·015	3	2·39	2·80	0·024	0·028
1·020	4	3·17	3·70	0·033	0·038
1·025	5	3·94	4·60	0·040	0·047
1·030	6	4·71	5·50	0·049	0·057
1·035	7	5·47	6·38	0·057	0·066
1·040	8	6·22	7·26	0·064	0·075
1·045	9	6·97	8·13	0·073	0·085
1·050	10	7·71	8·99	0·081	0·094
1·055	11	8·43	9·84	0·089	0·104
1·060	12	9·15	10·68	0·097	0·113
1·065	13	9·87	11·51	0·105	0·123
1·070	14	10·57	12·33	0·113	0·132
1·075	15	11·27	13·15	0·121	0·141
1·080	16	11·96	13·95	0·129	0·151
1·085	17	12·64	14·74	0·137	0·160
1·090	18	13·31	15·53	0·145	0·169
1·095	19	13·99	16·32	0·153	0·179
1·100	20	14·67	17·11	0·161	0·188
1·105	21	15·34	17·89	0·170	0·198
1·110	22	16·00	18·67	0·177	0·207
1·115	23	16·67	19·45	0·186	0·217
1·120	24	17·34	20·23	0·195	0·227
1·125	25	18·00	21·00	0·202	0·236
1·130	26	18·66	21·77	0·211	0·246
1·135	27	19·32	22·54	0·219	0·256
1·140	28	19·98	23·31	0·228	0·266
1·145	29	20·64	24·08	0·237	0·276
1·150	30	21·29	24·84	0·245	0·286
1·155	31	21·94	25·60	0·254	0·296
1·160	32	22·60	26·36	0·262	0·306
1·165	33	23·25	27·12	0·271	0·316
1·170	34	23·90	27·88	0·279	0·326
1·175	35	24·54	28·63	0·288	0·336
1·180	36	25·18	29·38	0·297	0·347
1·185	37	25·83	30·13	0·306	0·357
1·190	38	26·47	30·88	0·315	0·367
1·195	39	27·10	31·62	0·324	0·378

Specific Gravities at $\frac{15^\circ}{4^\circ}$.	Degrees Twad.	100 parts by weight contain		1 litre contains kg.	
		N_2O_5.	HNO_3.	N_2O_5	HNO_3.
1·200	40	27·74	32·36	0·333	0·388
1·205	41	28·36	33·09	0·342	0·399
1·210	42	28·99	33·82	0·351	0·409
1·215	43	29·61	34·55	0·360	0·420
1·220	44	30·24	35·28	0·369	0·430
1·225	45	30·88	36·03	0·378	0·441
1·230	46	31·53	36·78	0·387	0·452
1·235	47	32·17	37·53	0·397	0·463
1·240	48	32·82	38·29	0·407	0·475
1·245	49	33·47	39·05	0·417	0·486
1·250	50	34·13	39·82	0·427	0·498
1·255	51	34·78	40·58	0·437	0·509
1·260	52	35·44	41·34	0·447	0·521
1·265	53	36·09	42·10	0·457	0·533
1·270	54	36·75	42·87	0·467	0·544
1·275	55	37·41	43·64	0·477	0·566
1·280	56	38·07	44·41	0·487	0·568
1·285	57	38·73	45·18	0·498	0·581
1·290	58	39·39	45·95	0·508	0·593
1·295	59	40·05	46·72	0·519	0·605
1·300	60	40·71	47·49	0·529	0·617
1·305	61	41·37	48·26	0·540	0·630
1·310	62	42·06	49·07	0·551	0·643
1·315	63	42·76	49·89	0·562	0·656
1·320	64	43·47	50·71	0·573	0·669
1·325	65	44·17	51·53	0·585	0·683
1·330	66	44·89	52·37	0·597	0·697
1·335	67	45·62	53·22	0·609	0·710
1·340	68	46·35	54·07	0·621	0·725
1·345	69	47·08	54·93	0·633	0·739
1·350	70	47·82	55·79	0·645	0·753
1·355	71	48·57	56·66	0·658	0·768
1·360	72	49·35	57·57	0·671	0·783
1·365	73	50·13	58·48	0·684	0·798
1·370	74	50·91	59·39	0·698	0·814
1·375	75	51·69	60·30	0·711	0·829
1·380	76	52·52	61·27	0·725	0·846
1·385	77	53·35	62·24	0·739	0·862
1·390	78	54·20	63·23	0·753	0·879
1·395	79	55·07	64·25	0·768	0·896
1·400	80	55·97	65·30	0·783	0·914
1·405	81	56·92	66·40	0·800	0·933
1·410	82	57·86	67·50	0·816	0·952
1·415	83	58·83	68·63	0·832	0·971
1·420	84	59·83	69·80	0·849	0·991
1·425	85	60·84	70·98	0·867	1·011
1·430	86	61·86	71·17	0·885	1·032
1·435	87	62·91	73·39	0·903	1·053
1·440	88	64·01	74·68	0·921	1·075
1·445	89	65·13	75·98	0·941	1·098
1·450	90	66·24	77·28	0·961	1·121
1·455	91	67·38	78·60	0·981	1·144
1·460	92	68·56	79·98	1·001	1·168
1·465	93	69·79	81·42	1·023	1·193

Specific Gravities at $\frac{15^\circ}{4^\circ}$.	Degrees Twad.	100 parts by weight contain		1 litre contains kg.	
		N_2O_5.	HNO_3.	N_2O_5.	HNO_3.
1·470	94	71·06	82·90	1·045	1·219
1·475	95	72·39	84·45	1·068	1·246
1·480	96	73·76	86·05	1·092	1·274
1·485	97	75·18	87·70	1·116	1·302
1·490	98	76·80	89·60	1·144	1·335
1·495	99	78·52	91·60	1·174	1·369
1·500	100	80·65	94·09	1·210	1·411
1·501	...	81·09	94·60	1·217	1·420
1·502	...	81·50	95·08	1·224	1·428
1·503	...	81·91	95·55	1·231	1·436
1·504		82·29	96·00	1·238	1·444
1·505	101	82·63	96·39	1·244	1·451
1·506	...	82·94	96·76	1·249	1·457
1·507	...	83·26	97·13	1·255	1·464
1·508	...	83·58	97·50	1·260	1·470
1·509	...	83·87	97·84	1·265	1·476
1·510	102	84·09	98·10	1·270	1·481
1·511	...	84·28	98·32	1·274	1·486
1·512	...	84·46	98·53	1·277	1·490
1·513	...	84·63	98·73	1·280	1·494
1·514	...	84·78	98·90	1·283	1·497
1·515	103	84·92	99·07	1·287	1.501
1·516	...	85·04	99·21	1·289	1·504
1·517	...	85·15	99·34	1·292	1·507
1·518	...	85·26	99·46	1·294	1·510
1·519	...	85·35	99·57	1·296	1·512
1·520	104	85·44	99·67	1·299	1·515

Correction of the observed specific gravities for temperatures a little above or below 15° C.

					Add for − 1° C. Deduct for + 1° C.
With sp. gr. between		1·000	to	1·020	0·0001
"	"	1·021	"	1·040	0·0002
"	"	1·041	"	1·070	0·0003
"	"	1·071	"	1·100	0·0004
"	"	1·101	"	1·130	0·0005
"	"	1·131	"	1·160	0·0006
"	"	1·161	"	1·200	0·0007
"	"	1·201	"	1·245	0·0008
"	"	1·246	"	1·280	0·0009
"	"	1·281	"	1·310	0·0010
"	"	1·311	"	1·350	0·0011
"	"	1·351	"	1·365	0·0012
"	"	1·366	"	1·400	0·0013
"	"	1·401	"	1·435	0·0014
"	"	1·436	"	1·490	0·0015
"	"	1·491	"	1·500	0·0016
"	"	1·501	"	1·520	0·0017

A controversy on the specific gravities of nitric acid arose in 1905 between Winteler and Lunge. Winteler (*Chem. Zeit.*, 1905, p. 689) asserted that in Lunge and Rey's table errors occurred up to 2·5 per cent., and he gave a new table of his own. Lunge (*ibid.*, 1905, p. 933) replied to Winteler, refuting all the objections made by this chemist to Lunge and Rey's table, and pointing out that the latter agrees very well with the tables of Veley and Manley (*J. Soc. Chem. Ind.*, 1903, p. 1227), and of Ferguson. Winteler replied to this (*Chem. Zeit.*, 1905, p. 1009), and Lunge made a final reply (*ibid.*, p. 1072) which put an end to the controversy.

A table of the specific gravities of nitric acid by Putzer (*Chem. Zeit.*, 1905, p. 1222) so nearly agrees with that of Lunge and Rey that it is unnecessary to repeat it here. Exactly the same holds good of the table given by W. C. Ferguson in *J. Soc. Chem. Ind.*, 1905, p. 788. *Cf.* also Veley, *Chem. News*, 1911, civ. p. 309.

Loring Jackson and Wing, and a little later on R. Hirsch (*Chem. Zeit.*, 1888, p. 911), have shown that the presence of *lower oxides of nitrogen* in nitric acid has a considerable influence on its specific gravity. Thus the first runnings from a distillation possessed a sp. gr. = 1·62, but contained 12 per cent. by weight of HNO_2. Hirsch assumes (without strict proof) that every per cent. of HNO_2 raises the specific gravity by 0·01. If this were correct, an acid of sp. gr. 1·44, but containing 1 per cent. HNO_2, would really contain only 99 per cent. of HNO_3 of sp. gr. 1·43. Now 100 g. of pure acid of 1·44 are = 74·4 g. HNO_3, but 99 g. of 1·43 only = 71·0; hence the 1 per cent. of HNO_2 present makes a difference of 3·4 per cent. of HNO_3 in the real strength, compared with the apparent strength as taken from the specific-gravity tables.

This subject has been more accurately investigated by Lunge and Marchlewski. From their paper (*Z. angew. Chem.*, 1892, p. 10) I give the following table (see p. 138), showing this influence in the case of nitric acid of sp. gr. 1·4960 $\left(\text{at } \frac{15^\circ}{4^\circ}\right)$.

Saposchnikoff (*Chem. Centr.*, 1900, ii. p. 708, and 1901, ii. p. 1330) has studied the conditions of equilibrium between HNO_3, HNO_2, and NO, *i.e.*, the formation of HNO_3 and NO from HNO_2, and the reduction of HNO_3 by NO to HNO_2.

Schaller (*Chem. Zeit.*, 1904, p. 594) found in commercial fuming nitric acid from 7·5 to 13·7 per cent. lower nitrogen oxides, calculated as N_2O_4, and from 0·5 to 8·1 per cent. H_2SO_4.

An investigation on the conditions of the equilibrium among nitric acid, nitrous acid, and nitric oxide has been made by Lewis and Edgar (*J. Amer. Chem. Soc.*, 1911, xxxiii. pp. 292-299).

N_2O_4 per cent.	Alteration of sp. gr. of nitric acid by N_2O_4.	N_2O_4 per cent.	Alteration of sp. gr. of nitric acid by N_2O_4.
0·25	0·00050	6·75	0·04475
0·50	0·00075	7·00	0·04650
0·75	0·00150	7·25	0·04720
1·00	0·00300	7·50	0·05000
1·25	0·00475	7·75	0·05165
1·50	0·00675	8·00	0·05325
1·75	0·00775	8·25	0·05500
2·00	0·01050	8·50	0·05660
2·25	0·01250	8·75	0·05825
2·50	0·01425	9·00	0·06000
2·75	0·01625	9·25	0·06160
3·00	0·01800	9·50	0·06325
3·25	0·01985	9·75	0·06500
3·50	0·02165	10·00	0·06600
3·75	0·02350	10·25	0·06815
4·00	0·02525	10·50	0·06975
4·25	0·02690	10·75	0·07135
4·50	0·02875	11·00	0·07300
4·75	0·03050	11·25	0·07450
5·00	0·03225	11·50	0·07600
5·25	0·03365	11·75	0·07750
5·50	0·03600	12·00	0·07850
5·75	0·03775	12·25	0·08050
6·00	0·03950	12·50	0·08200
6·25	0·04175	12·75	0·08350
6·50	0·04300		

Mixtures of nitric and sulphuric acid have been studied by Saposchnikoff (*Chem. Centr.*, 1904, i. p. 1322; ii. pp. 396 and 685). He observed the partial pressure of HNO_3 in mixtures made with increasing quantities of H_2SO_4, the composition of the vapours carried away by air at 25°, the density of these vapours, and their specific conductivity. His observations proved that no chemical compound of nitric and sulphuric acid is formed, but in the case of a large quantity of sulphuric acid some anhydrous N_2O_5 is formed. The vapour pressure of nitric acid is reduced by the addition of sulphuric acid; the vapours consist at first of pure HNO_3, later on partly of N_2O_5. He also determined the specific gravities of such mixtures and their specific conductivity. The specific gravity shows a maximum at about 90 per cent. H_2SO_4, owing to the formation of N_2O_5; above 90 per cent. H_2SO_4 the density decreases owing to the interaction of H_2SO_4 with the nitrogen oxides. A continuation of this work was published by the same author in 1905 (*Chem. Centr.*, 1905, ii. pp. 381 and 1152; *J. Soc. Chem. Ind.*, 1905, p. 1031). In all these mixtures the vapours consist of pure HNO_3; hence the admixture of sulphuric acid increases the concentration of the nitric acid, and makes its nitrating action more energetic. The composition of the mixture, possessing the highest vapour tension, is: $5HNO_3+2H_2SO_4+3H_2O$.

The *oxidising properties* of nitric acid are well known and cannot be described in detail here; but it should be mentioned that an acid containing the lower oxides of nitrogen, such as the "red fuming nitric acid," has even more strongly oxidising properties than the pure acid, and this helps to explain some points in the theory of the formation of sulphuric acid, as we shall see in a subsequent chapter.

Reynolds and Taylor (*Chem. News*, 1911, civ. p. 315) examined the decomposition of nitric acid by the action of *light.*

Manufacture of Nitric Acid.

This acid has been known since the times of Geber, in the eighth century; and Raymundus Lullus in 1225 taught how to prepare it by distilling a mixture of clay and saltpetre. Nowadays it is always made by distilling nitrate of soda with sulphuric acid, an excess of the latter acid beyond the theoretica quantity being used in practice. The equation: $2NaNO_3+H_2SO_4=2HNO_3+Na_2SO_4$, in theory requires for 85 parts of $NaNO_3$ 49 parts of SO_4H_2, and yields $63NO_3H$ along with $71Na_2SO_4$; this comes to the same as 57·6 parts of SO_4H_2, or, say, 60 parts of ordinary strong oil of vitriol (with 95 per cent. of SO_4H_2) to 100 parts of 95-per-cent. nitrate. If these proportions are used, a portion of the nitric acid is always decomposed into O and N_2O_4, and red fuming acid is obtained. This arises from the fact that the above equation is only realised at a high temperature, whilst at less elevated temperatures sodium bisulphate is formed: $NaNO_3+H_2SO_4=HNO_3+NaHSO_4$. Moreover, the presence of strong sulphuric acid, owing to its attraction for the elements of water, has a tendency to split up some HNO_3 into H_2O and N_2O_5, the latter compound being at once decomposed into N_2O_4 and O. To avoid the loss involved in this operation, generally more dilute nitric is produced by employing weaker sulphuric acid, say of 140° to 148° Tw., and more than the theoretical quantity of it, generally from 20 to 30 per cent. in excess of the simple equivalent. In this case the admixture of a certain quantity of sodium bisulphate makes the residue of distillation much more easily fusible and facilitates its removal from the retorts. When the acid is made at factories where salt is decomposed, even more sulphuric acid than the above is generally employed, as the excess is not lost, the residual "cylinder-cake" or "nitre-cake" being regularly mixed with the salt to be decomposed in the sulphate-pans; in this case as much sulphuric acid is saved as corresponds to the bisulphate contained in the cylinder-cake.

Nitric acid was formerly made in glass retorts, but nowadays cast-iron retorts are universally employed. The retorts belong mainly to two different types—horizontal cylinders, charged sideways, and pots or stills, charged from the top.

The ordinary type of French cylinder apparatus, used in many places outside of France as well, is represented in Figs. 11 and 12 on a scale of 1 : 25. The ends of the cylinders are here exposed to the air and consist of cast-iron disks, 1½ in. thick, cemented into the rebates cast on to the ends of the cylinder by the usual rust cement (100 iron filings, 5 flowers of sulphur, 5 sal-ammoniac), or by a mixture of this with ground fire-bricks and the like. At all events the back end is fixed in this way, and is provided with a pipe for taking away the vapours; the other end is made to take off and serves for charging the nitre and discharging the residue. A hole and S-shaped funnel in the man-lid allow of running in the sulphuric acid. These cylinder-ends cause a good deal of cooling, and consequently a loss of fuel, which can be avoided to a great extent if they are not made of iron but of a single stone flag each; the charging-end also remains fixed in this case, the nitre being charged through a small general opening in it, and the residue being run off in a liquid state through a pipe generally closed by a ground-in iron stopper. A little more sulphuric acid is employed in this case, so as to obtain a very fluid mass at the end. If sulphuric acid of

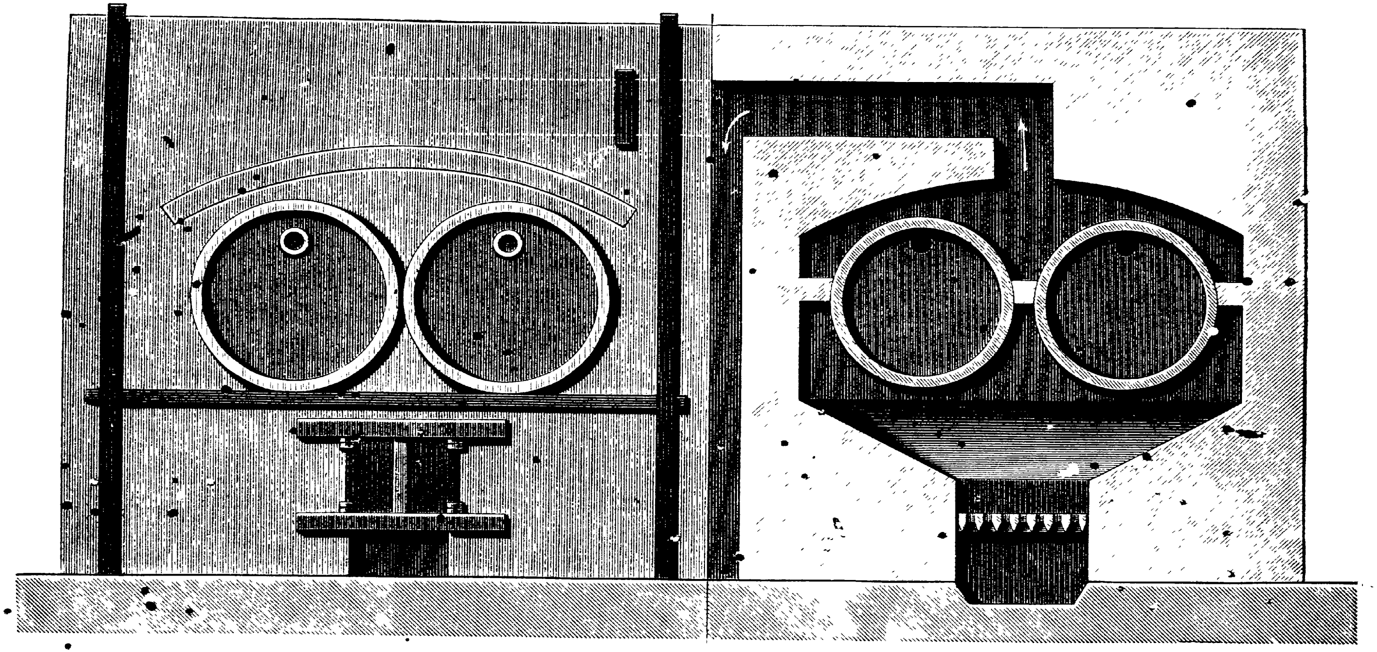

FIG. 11.

144° Tw. is employed, the receivers will contain nitric acid of 77° to 82° Tw.; if weaker acid is desired, a little water is put into the receivers. The strongest acid, of 100° Tw., can only be made from strong vitriol and dried nitrate.

At first the cylinders are fired rather strongly; but as soon as the first receivers get warm the fire is slackened, and during eighteen hours is kept so that of eight receivers only the first five are warm to the touch. If the heat gets up too high, the contents of the retort may boil over, and far more ruddy vapours will be formed. The end of the reaction is known by the cooling of the receivers; then the fire is increased again for a little time, and at last is allowed to go down.

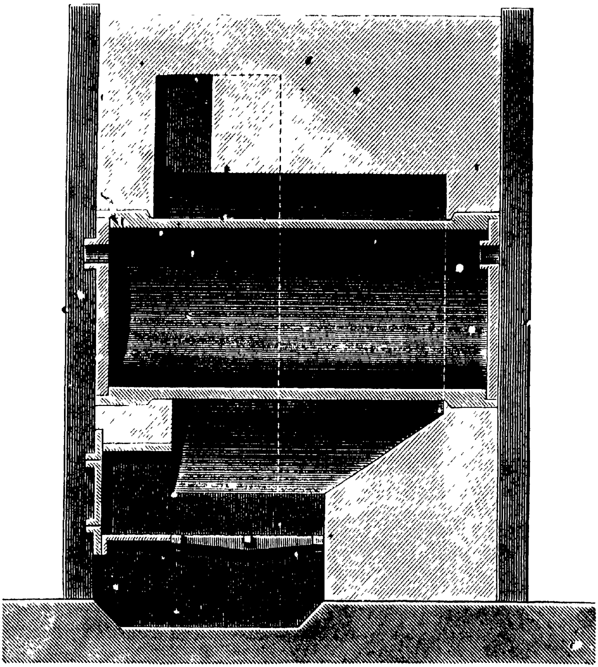

FIG. 12.

In regular work, some red vapours are formed at first, but much less with rather weaker acid (say 135° Tw.) than with stronger acid. At the end the red or yellow vapours appear again and last up to the finish.

The cylinders are sometimes cast so that their upper half can be protected against the attack of the acid by lining it with acid-proof bricks (see Fig. 13); but some believe that this does more harm than good, as the upper part of the metal cylinder is all the less acted upon by the nitric acid the hotter it becomes.

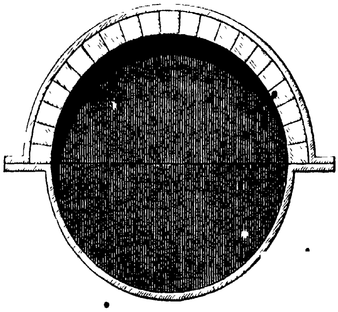

FIG. 13.

A more perfect form of cylinders is that employed at the Griesheim works, and shown in full detail in Figs. 14 to 17 with all the measurements marked in centimetres.[1]

These retorts work off 8 cwt. of nitre per twenty-four hours, with an expenditure of 2½ cwt. of coal or very little more, inclusive of the time of filling and emptying. In case of need, 25 per cent. more can be charged, without fear of boiling over, with careful work. Such boiling over occurs more easily with strong sulphuric acid (of 1·84 sp. gr.) than with weaker acid (140° Tw.). The setting is so arranged that the fire-gases entirely surround the cylindrical part, and the ends are made of sandstone slabs, cemented and kept in their places by iron bars pressing against them on the outside. In this kind of apparatus no corrosion takes place, wherefore the arrangement shown in Fig. 13 is quite unnecessary. The exit opening continues into a glass tube, forming connection with the condensing-apparatus. The arrangement for running off the nitre-cake is made quite clear in Fig. 14.

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[1] These figures are taken from Häussermann's article "Nitric Acid," in Muspratt-Bunte's *Enc. d. Techn. Chemie*, 4th edition, vii. pp. 651 *et seq.* Some notes from this article are also given in the following pages.

The objection sometimes made to cylindrical retorts, that

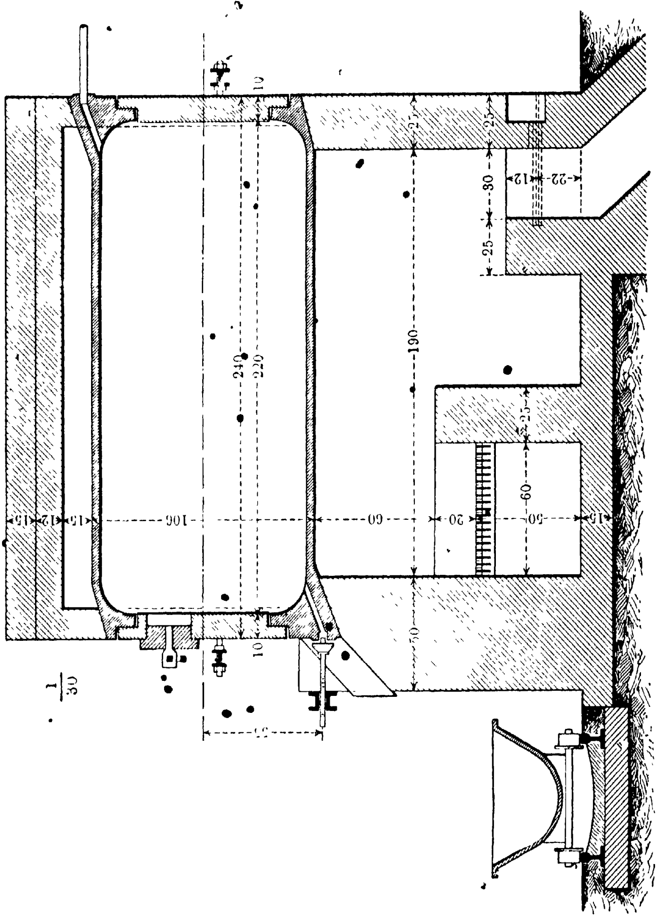

FIG. 14.—Longitudinal section.

they do not easily permit the manufacture of the strongest nitric acid, is refuted by the experience of many years at the various works belonging to the Griesheim Company.

The Società L. Vogel in Milan (B. P. 6846 of 1904) makes

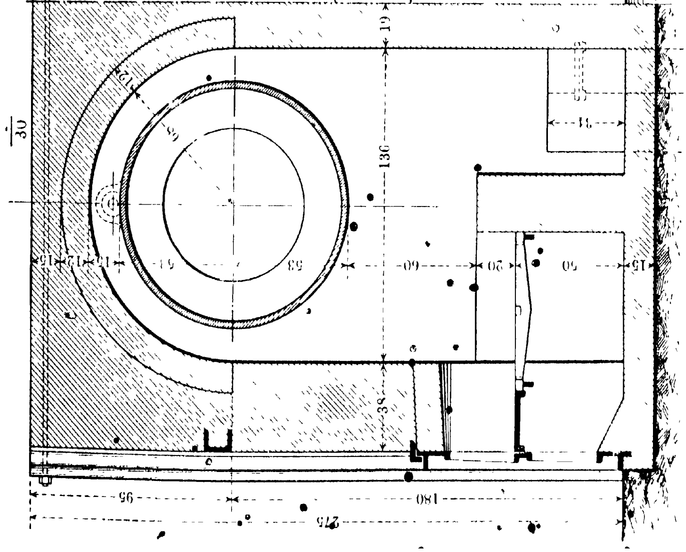

FIG. 15.—Sectional elevation.

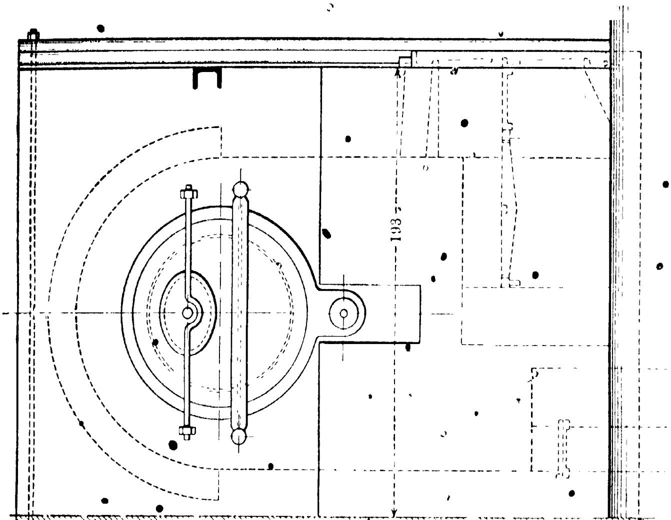

FIG. 16.—Front elevation.

nitric acid in cylinders placed in the dust-chambers of the pyrites kilns.

The other class of retorts, in the shape of pots or stills, is either entirely surrounded by the fire, or with its top exposed to the air. The former kind, as employed in France for very strong nitric acid, is shown in Fig. 18. It consists of cast-iron pots of from 4 to 5 ft. diameter and equal height, and a metal thickness of $1\frac{3}{4}$ to 2 in. (rather thicker at the bottom). There is a wide neck *a* at the top, closed by a lid, fastened on with a suitable cement, *e.g.* a mixture of clay and gypsum. There is a tube *b* for carrying away the gas, either coming out perpendicularly at the top, as shown here, or bending away horizontally, as in a laboratory retort; this tube should be

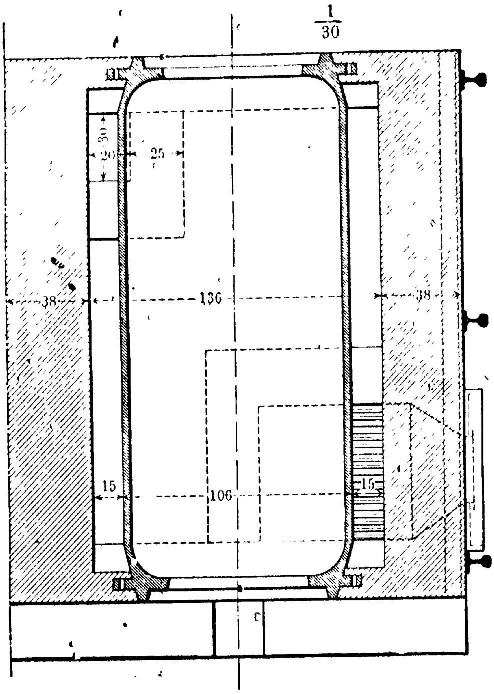

Fig. 17.—Sectional plan.

lined with an earthenware tube as far as it is at all liable to cool down below the point where the metal can be acted upon by nitric acid. Another tube *c* serves for introducing the sulphuric acid; this is preferable to running it in through the neck *a*, after charging the nitre. Sometimes there is no pipe provided for running out the liquid residue, but it is better to have one, as shown at *d*, and to protect this tube against the direct action of the fire by a fireproof covering. Where this is not provided, the liquid residue must be ladled out through *a* at the close of the operation, which is a disagreeable proceeding. The pot is set in a furnace so that it is altogether surrounded by the fire, even at the top, to which access is afforded for charging by lifting off a fire-clay slab, or a metal plate filled with ashes, as shown at *e*. By this means a saving of fuel is effected, and the equal heating of the retort causes it to stand the action of the nitric acid very well. A pot 5 ft. wide and 5 ft. high takes a charge of 9 cwt. of nitre, and requires from sixteen to eighteen hours to work this off, including the time for charging and emptying. Of this time, one hour may be reckoned for charging and making the joints, six hours for the first stage, where red fumes appear, about as much for the second stage, where the vapours are almost colourless, and four or five hours for the last stage, where the temperature has to be raised much higher, the yellow and red vapours appear again and more water comes over with the acid.

That kind of pot where the top (with the small hole) is exposed to the air is shown on a scale of 1 : 60 in Fig. 19. It forms part of the Valentiner vacuum system to be described below. The pot, for a charge of a ton of nitre, is composed of two parts. The outlet-pipe for the nitre-cake runs almost horizontally, so that it is easily cleaned. The gas-pipe first enters a small receiver, destined to keep back any froth carried over. Such a vacuum retort is finished in twelve hours, with about 4 cwt. of coal per ton of nitre.

A good *cement* for permanent joints against nitric acid in the retorts consists of 10 parts powdered volvic lava, 7 iron filings, 7 powdered brimstone, 7 fire-clay, 10 ground fire-bricks, moistened with as little water as possible. If carefully stemmed into the joint, it becomes very hard.

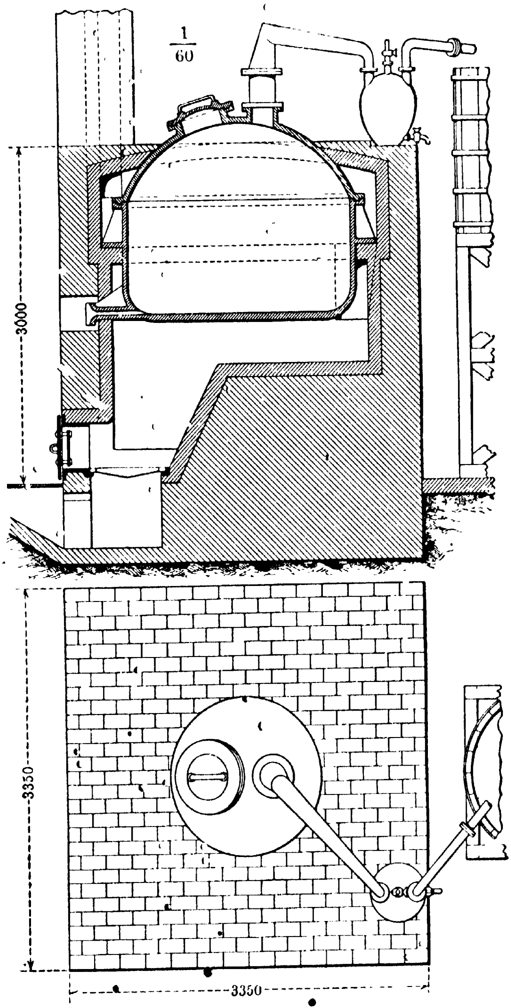

FIG. 19.

A cement for the earthenware pipes, etc., in the condensing-apparatus can be made from 5 parts hot linseed-oil, 2 parts brimstone, 2 parts india-rubber scraps, and enough sulphate of baryta to produce a thick paste, which is employed in the hot state.

The most universally employed cement for nitric acid (and other acids) is *asbestos cement.* Guttmann gives the following prescription for preparing it:—One part of the usual 33 per cent. solution of silicate of soda is dissolved in 19 parts water, and asbestos powder is kneaded with it, in small quantities at a time, until a tough paste is obtained. Should a cement be required which will become very hard, a little finely powdered barium sulphate is mixed with it; but this is not desirable where pipes have to be changed, as this cement cannot be removed without risk of damaging the pottery. If too little water is used from the first, the water absorbed by the cement will cause it to swell and to burst the sockets. The cement is applied in small bits, and tightly pressed in by means of a piece of wood with a blunt-ended tool. The surface is flattened and moistened with some silicate of soda solution. If the putty in the sockets shrinks, about ⅜ in. of it is raked out and fresh cement put in.

Asbestos cement must never be treated with pure water to begin with, but with acid or acid fumes, in order to ensure its setting by the separation of silica.

Sadtler (*Chem. Trade J*, xxxiv. p. 517) gives a general description of such cements or "lutes."

Guttmann (*J. Soc. Chem. Ind.*, 1908, p. 668) reports that nitric acid stills are now made much larger than formerly. Until lately, the largest still was of 2½ tons capacity, but he mentions a cylindrical still of several in use, each holding 5 tons, and speaks of one of a capacity of 10 tons nitrate of soda.

Figs. 20, 21, and 22, from drawings which I owe to the kindness of Mr H. H. Niedenführ, show the kind of still employed by Mr O. Guttmann in connection with his condensing-plant, but of course applicable in every other case. The drawings are to scale and are clear enough without further explanations. The brick setting, as arranged by Mr Niedenfuhr, has had an excellent effect, and admits of finishing a charge of 12 cwt. in twenty-four hours with only 17 per cent. of

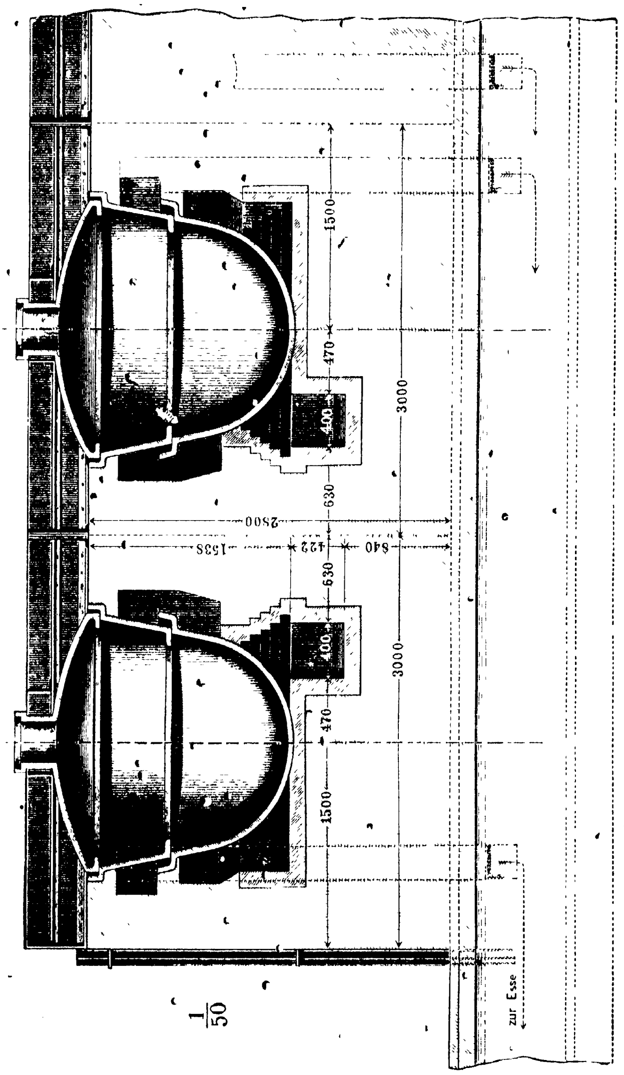
1500
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Fig 2c.

coal. The internal flanges have the effect of diverting the contents of the pot, when frothing, towards the centre, and of preventing any acid condensing from running down the sides.

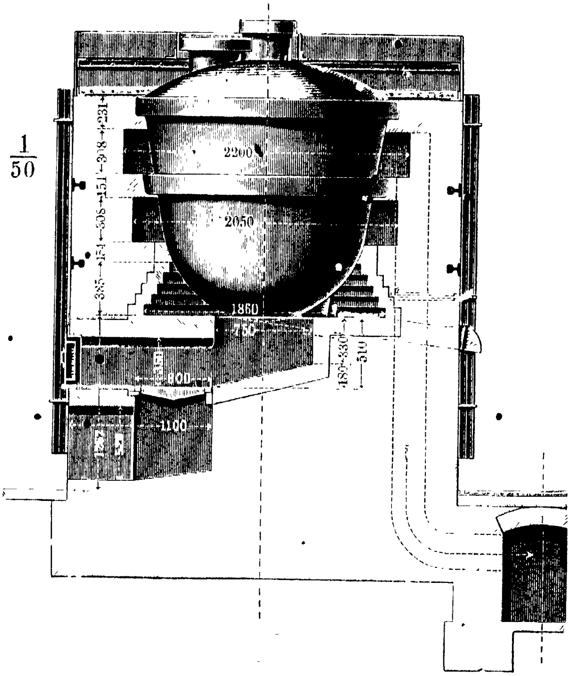

FIG. 21.

These retorts have been found specially useful for making a maximum of strong acid.[1]

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[1] Guttmann (*J. Soc. Chem. Ind.*, 1905, p. 1331) declares Niedenfuhr's statements and plans, as given above, to be unauthorised by him and incorrect, but he does not say what errors there are in them. In a letter to myself he stated the following defects in Niedenfuhr's plans. The fireplace is unnecessarily lined with fire-bricks; the bottom of the retort is not sufficiently heated. The bracing-rails outside are unnecessary. The running-off pipe for the bisulphate is sure to be leaky, and the placing of the wagons for it in the same room as the condensation is objectionable. The covers shown and intended for drying the nitre are wrongly arranged; Guttmann himself employs cast-iron plates, below which the last flue of the fire-gases produces sufficient heat (80°). If surrounded by these fire-gases on all sides, the iron

Usually it is preferred to cast such conical pots in one piece (like caustic-soda pots), and to set them so that the cover projects over the brickwork. In order to keep the cover sufficiently hot, it is covered by a layer of ashes or by bricks; the drying of the nitre in this case is equally performed by the waste heat of the fire, but in a separate place at the end of the retort-bench.

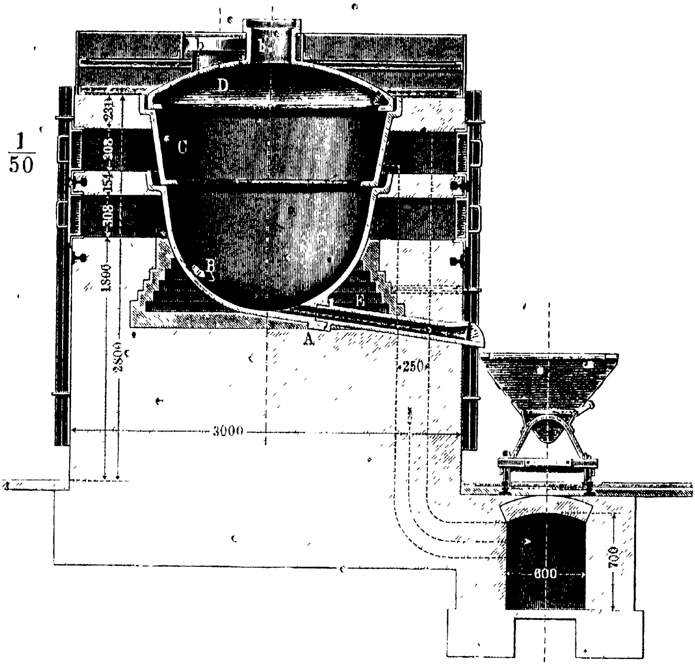


FIG. 22.

According to notes from actual practice, the nearly cylindrical middle part of the Guttmann retorts (see Figs. 20 to 22) lasts practically for ever. The bottom parts may last up to ten years, the covers about one year. The latter are surrounded with a

plates stand for many years. He builds his retorts for charges of 1 ton each, worked off in twelve to fourteen hours, including the charging, discharging, and cooling; recently he goes even up to retorts for 2½ tons, which are easily managed by a condensing-battery of twelve pipes.

sheet-iron rim and serve for drying the nitre. [It would seem preferable to me, on the contrary, to avoid any condensation inside the covers by protecting them against cooling by brickwork or otherwise, and to effect the drying of the nitre by means of the waste heat from the retort fires.] Each retort receives a charge of 12 cwt. nitre and 13 cwt. sulphuric acid (95 per cent.), which is worked off in fourteen hours with only 8 cwt. of coal. The nitre-cake is run off at once, and the retort is ready for charging again after cooling for an hour. A set of 10 retorts is worked by two shifts of three men each; the men have also to wheel the nitre from the storehouse and to manage the condensation.

At some works they use large semicylindrical troughs of cast metal with broad flanges and a vertical rim all round, in order to cover them by a brick arch or a stone slab. At others they employ large pots with rounded bottom, lying on their side: the open end, which forms part of the front of the furnaces, being closed by a stone slab. Neither of these forms has found very much favour elsewhere.

Prentice (B. P. 6960 of 1893; Ger. P. 79645) carries on the process in a continuous manner. The nitre is mixed with sulphuric acid outside the retort, preferably in a kind of mortar-mill (according to B. P. No. 8902 of 1893, a large excess of sulphuric acid should be employed and the residue subsequently used for the manufacture of superphosphate). The mud thus produced is conveyed into a heated chamber in which the nitrate dissolves in the sulphuric acid, but no nitric acid is as yet split off [?]; here chlorine and nitrogen tetroxide are liberated and escape into a condensing-apparatus. Owing to this the nitric acid is later on free from volatile impurities [?]. The mixture is now charged into the retort, which has an oblong section and is divided into a number of separate chambers by partitions starting from the cover and not reaching entirely to the bottom. Above each chamber the cover is provided with a head and vapour-pipe. The retort is heated from below, and the fire-gas subsequently travels round the sides. The mixture coming from the heating-chamber enters the first chamber of the retort, where it begins to boil and gives off a large quantity of strong nitric acid mixed with a little nitrogen tetroxide. The mixture now, without ceasing to boil, flows on from chamber to chamber, giving off pure nitric acid, which gets weaker and weaker in the following chambers. In the last chamber, placed immediately above the fire, the temperature is highest; here the last nitric acid is driven off, together with much water and a little sulphuric acid, and the nitre-cake is drawn off, free from the nitrate. By this method two-fifths of the fuel and four-fifths of the condensing-plant [?] can be saved. A still producing 4 tons per week weighs less than 2 tons. A communication by Prentice in the *J. Soc. Chem. Ind.*, 1894, p. 323, gives nothing new. In discussing it doubts were expressed as to whether that process is applicable at such works where the residue cannot be utilised for the manufacture of superphosphate, as it contains a large excess of acid. Indeed, this extra quantity of acid required for working that otherwise very ingenious process has made it an economical failure.

Uebel (patents of the Chemische Fabrik Rhenania, B. P. 27240 of 1898, and 3305 of 1901) proceeds in a novel way for the manufacture of nitric acid. The nitre-cake, running out at a high temperature from the retorts, is mixed with sulphuric acid of about 1·71 sp. gr. in such proportions that a "polysulphate" is formed, the water being evaporated by the heat remaining in the nitre-cake. This polysulphate, of the composition $= NaH_3(SO_4)_2$, serves instead of fresh sulphuric acid for manufacturing the next batch of nitric acid, in which case the latter is obtained of the highest strength just as if the strongest sulphuric acid had been employed. Of course the fresh nitre-cake formed from the second operation amounts to much more than that from the first; therefore a portion of it is set aside in the ordinary manner, and the remainder is again employed for making nitric acid. The practical work carried out with this process has led to the construction of a new and original style of retorts, which may be very usefully adopted even when nitrate of soda is to be decomposed in the ordinary way by sulphuric acid, not by "polysulphate."

The principal advantages of the new process are: that the alternate heating and cooling of the apparatus is avoided, which produces a saving in fuel and prolonged duration of the plant; that there is not the same inequality of the nitric acid as is produced during the period of working off a retort on the old system; that a much smaller and consequently much cheaper plant and only half of the ordinary ground-space are required for the same output, both for distillation and condensation (the Uebel plant may be combined with any of the systems of condensation to be described below); that there is less labour required; and that the strongest acid can be made by means of ordinary sulphuric acid 140° Tw., as its water is evaporated free of expense in the formation of the polysulphate—"waste-acid" from nitrating processes being equally fit for employment.

The Uebel process is illustrated in Figs. 23 to 25. Two

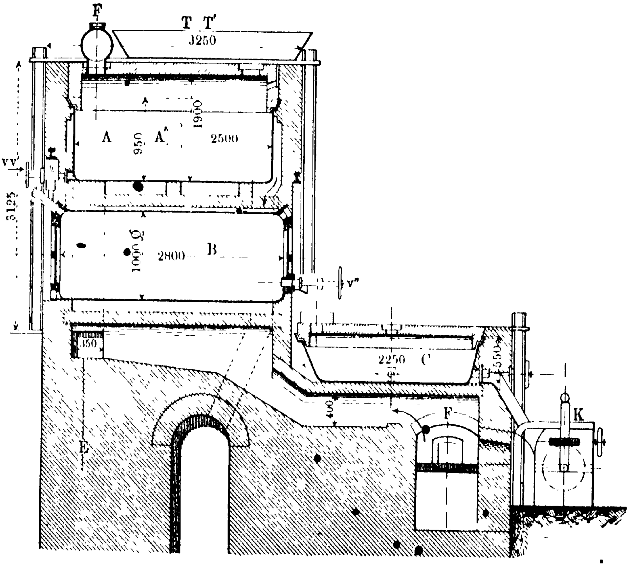
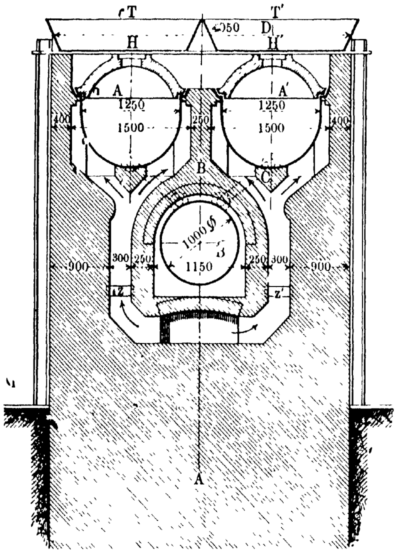


FIG. 23.

parallel retorts A, A′ (consisting of a cast-iron bottom piece and a stone or stoneware cover) are alternately charged with nitrate of soda and the requisite quantity of liquid "polysulphate" (or else, if there is a sufficient quantity of *strong* acid at disposal, *e.g.*, where manufacturing by contact processes, directly with such acid). The heating is performed by the waste fire-gases of the lower retort B, a temperature of 170° to 200° C. being thus attained in A and A′. When most of the nitric acid has been expelled, the contents of A and A′ are let down into retort B, where the last portion of nitric acid is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T'
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D
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H'
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1250
1250
1500
1500
400
400
250
B
C
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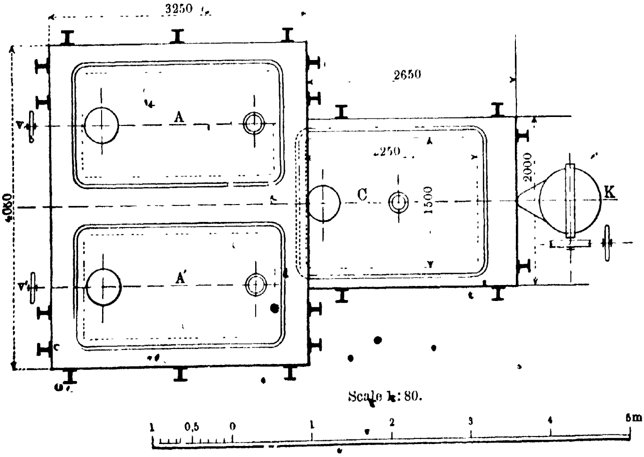
300
250
250
300
900
900
Z
Z'
A

FIG. 24.


3250
2650
A
A'
C
K
4050
2250
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2000
V
V'
Scale 1:80.
1
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2
3
4
5m

FIG. 25.

liberated, at a temperature of about 300° C. The contents of B have, of course, been previously run out, but never completely, leaving always a stock of hot liquid "bisulphate" in the retort. The bisulphate (nitre-cake) is run from B into the cast-iron pan C, where it is mixed with previously heated sulphuric acid of about 140° Tw. (or with waste acid from nitrating processes of equal strength) in the proportion of forming a tetrasulphate, H_2SO_4, $NaHSO_4$. In consequence of the high temperature of the liquid nitre-cake, the water present in the fresh sulphuric acid is evaporated (together with any nitric acid present in waste acids, if such are employed) and is carried away by a pipe, or a vapour hood, not shown in the drawing. Half of the "polysulphate" formed in C is employed for a fresh operation in A, A′, the other half being at disposal for any outside utilisation in lieu of highly concentrated acid. If such utilisation is not possible, half of the nitre-cake is run out from C *before* adding fresh sulphuric acid and only the other half is employed for making "polysulphate," the unemployed half being utilised in the manner followed in other cases.

(An English patent by Claes, No. 1072 of 1900, describes the manufacture of "polysulphates" from nitre-cake and sulphuric acid as a commercial article.)

The flame of the hearth F first heats retort B, which is protected by an arch, and then, according to the position of the damper, either A or A′. *v*, *v′* are valves for discharging the contents of A, A′ into B; *v″* another valve for discharging B into C, placed high enough to leave a stock of liquid nitre-cake in B.

After heating-up, A is charged with 8 cwt nitrate of soda, previously dried on the shallow basins T, T′ on the top of the furnace. The charging is performed through manholes H, H′, which are afterwards closed by covers and kept tight by nitrate of soda heaped upon them. Then fused polysulphate is gradually run in through a swan-neck pipe from the tilting-box K, previously lifted to the top of the furnace. This polysulphate will be at a temperature of about 120° or 130°, and must therefore be gradually introduced within from half an hour to an hour, so as to avoid a tumultuous evolution of nitric acid. Of course, in lieu of this, fresh acid can be employed, as stated above. During the introduction of the hot polysulphate damper *z* is closed and *z'* is opened; when finished, *z* is opened so that the fire-gases play upon A. When the temperature has risen to about 170°, nearly all HNO_3 has been driven out; the thin, liquid melt contains a little nitrate and all the water introduced with the nitrate and the polysulphate or fresh acid. It is now slowly run through valve *v* into retort B, where it meets with a stock of hot bisulphate. Here, without the frothing taking place in the old, directly fired, retorts, the last nitric acid and the water is drawn off within a very short time. The contents of B remain there until the contents of A' (which has been charged and worked in the meantime) are ready to be run off, which takes from three and a half to four hours. Then B is discharged into C, where fresh acid is run in as before described, so that room is made in B for receiving the contents of A'. Retort A in the meantime has been left empty for an hour, damper *z* being closed, in order to cool down. Now the polysulphate is run out of C into the tilting-box K, which is hoisted up to serve as before. Thus a charge of 8 cwt. of nitrate can be worked off in each of the retorts A and A' every four hours.

According to Hasenclever (*J. Soc. Chem. Ind.*, 1911, p. 1293), Uebel's three-boiler apparatus has been adopted in many cases. It secures material savings in space and fuel. The apparatus treats 1800 kg. nitrate of soda in twenty-four hours (*J. Soc. Chem. Ind.*, 1911, p. 1293).

The Chemische Fabrik Griesheim-Elektron (Ger. P. 170532) modifies the ordinary nitric-acid process as follows. Nitrate of soda and sulphuric acid are gradually introduced into the retort at the same time, but in separate places, with exclusion of air, in such manner that the temperature in the retort remains always above 140°. This avoids distillation by jumps, frothing over, and the necessity of cooling of the retort for a fresh charge, and lessens the wear and tear of the retort, and of the stoneware apparatus. (This process has been worked for some time at Offenbach, but the patent has been dropped.)

Valentiner and Schwarz (Fr. P. 374902 and U.S. P. 920224), in the manufacture of nitric acid under diminished pressure, restrict the passage between the retort and the condensing-coil to half the diameter of that coil. The higher pressure thus maintained in the retort prevents the uprush of sodium nitrate through the superincumbent sulphuric acid, which causes the distillation to progress more rapidly. The condensing-coil extends to the bottom of the first of a series of receivers, so as to form a liquid seal and gases, as lower nitrogen oxides and HCl pass on, leaving pure nitric acid behind.

The Badische Anilin- und Sodafabrik (Ger. P. 227377) manufacture nitric acid in a continuous way. The mixture of sodium nitrate and sulphuric acid passes through a series of stills which are heated each by itself to various degrees, and in which the contents are kept in mechanical motion. The outlet pipes for the vapours are shaped as siphons, and the vapours are separately condensed. With a series of 5 stills, the temperatures and strengths of acid, etc., are as follows:—

	Temperature. Degrees.	Strength of acid	
Still No. 1 .	110 to 120	96 to 97 per cent.	(60 per cent. of the total acid).
,, 2 .	150 ,, 170	88 ,, 90 ,,	
,, 3 .	210 ,, 250	60 ,,	
,, 4 .	250 ,, 280	2 ,, 5 ,,	
,, 5 .	280 ,, 300		

Schellhaass (Ger. P. 241711) also makes nitric acid in a continuous way. Sulphuric acid and fused nitrate of soda are separately introduced as a spray into a tower-like retort, kept at a temperature of 180°. In this retort the materials float about and are thoroughly mixed, so that the reaction is quite complete. Nitric acid of high concentration distils over the sodium bisulphate, which contains some nitric acid, is collected in a second retort, heated to about 300°, from which a more dilute nitric acid distils off.

Winteler (*Chem. Zeit.*, 1905, p. 820) gives the following rules for obtaining nitric acid of the highest concentration, and a good yield of it. (1) Keep the temperature of distillation as low as possible. (2) Do not allow the contents of the retort to be overheated anywhere. (3) Heat slowly enough to avoid this. (4) The most highly concentrated nitric acid, with best yield, is not obtained by employing highly concentrated sulphuric acid and dried nitrate, but with sulphuric acid of about 92 per cent. (5) The yield of concentrated nitric acid is raised by a supply of atmospheric oxygen in the retort. (6) It is useful to cool down the distilling gases as quickly as possible. In the distillation, aqueous nitric acid, which possesses a higher boiling-point than concentrated acid, is condensed before the stronger acid; hence by fractionated cooling acids of various concentration can be obtained. Guttmann (*ibid.*, p. 934) points out some errors of Winteler's, and the latter replies, *ibid.*, p. 1010.

The Chemische Werke vorm. Byk (Ger. P. 208143 and 217476) dissolve crystallised calcium nitrate in concentrated sulphuric acid, heat to 100°, and separate the nitric acid from the gypsum by pressing or centrifuging. If the nitric acid is no stronger than 59 per cent., the gypsum comes out in a perfectly hydrated form.

The *gases and vapours evolved during the working of the retorts*, apart from the vapour of nitric acid itself, consist of aqueous vapour, nitrogen peroxide, hydrogen chloride (which is, however, almost entirely converted into the following gases), chlorine, nitrosyl chloride, and a little iodine. HCl and the gases derived from it (NOCl and Cl) are principally formed at the commencement, through the decomposition of sodium chloride; but towards the end they appear again, owing to the decomposition of perchlorate. All of these impurities are dissolved by cold nitric acid, and hence occur in ordinary "unbleached" nitric acid.

Volney (*J. Amer. Chem. Soc.*, 1891, xiii. p. 246) showed that the frothing in the ordinary nitric-acid process takes place only in the last stage, when the strong acid has passed over and when the last portion of the nitre is suddenly acted upon, with formation of weaker acid. At this period practically only $NaHSO_4$ is in the retort besides $NaNO_3$.

Later on (*ibid.*, 1901, p. 489) Volney returned to this subject, with the following results. During the first period of the process, when the temperature of the retort is not above 100°, the compound $NaH_3(SO_4)_2$ is formed, which Volney calls "trisulphate" (it is really a tetrasulphate and identical with Uebel's "polysulphate," p. 117), by the reaction:

$$NaNO_3 + 2H_2SO_4 = NaH_3(SO_4)_2 + HNO_3.$$

The second period sets in at 100° and ends at 121°; here the principal reaction is:

$$NaNO_3 + NaH_3(SO_4)_2 = 2NaHSO_4 + HNO_3.$$

During the first period pure nitric acid, boiling between 81° and 88°, distils over. During the second period the HNO_3 begins to decompose into lower oxides and H_2O, so that more dilute acid must now be formed.

Later again (*J. Soc. Chem. Ind.*, 1901, p. 544; *cf.* also *J. Amer. Chem. Soc.*, 1902, p. 226), Volney states that the first phase, where acid of 77° to 90° boiling-point comes over, takes place at a temperature of 97° to 122°; the second phase, where acid of sp. gr. 1·505, boiling at 94° to 100°, comes over, requires a temperature in the retort of 130° to 165°. Above this the decomposition of HNO_3 sets in and yellow acid comes over. All this refers to working under ordinary pressures. When, however, working at reduced pressure on the Valentiner system (originally proposed by me, cf. *infrà*), say at 300 mm., the first stage runs from 55° to 100°, the boiling-point of the strongest acid at that pressure being only 45° to 75°; the second stage, where the polysulphate acts upon more nitrate, begins at 100° and is finished at 120°, instead of at 165° at ordinary pressure.

[In considering Volney's results, we must not overlook that they were obtained in glass vessels on a small scale. On the manufacturing scale, and working in iron vessels, higher temperatures cannot be avoided and the formation of nitrous vapours is proportionately increased. The frothing at the last stage of the distillation is generally ascribed to the partial decomposition of sodium bisulphate into pyrosulphate and water: $2NaHSO_4 = Na_2S_2O_7 + H_2O$.]

In a subsequent paper (*J. Soc. Chem. Ind.*, 1901, p. 1189) Volney gives the results of working at a much stronger vacuum, viz., 110 mm. absolute pressure. During the first phase, at about 74°, free sulphuric acid acted on the nitrate; during the second phase, at about 85°, the polysulphate did the principal action. The outside temperature rose to 140°. The distilling nitric monohydrate boiled at 30°. With concentrated sulphuric acid there is a great amount of frothing, which does not take place with acid of 60° B. When working with such acid at ordinary pressure, the greatest portion of the nitric acid distils at about 118° without frothing; at a pressure of 110 mm. at 74°, with slight frothing. In both cases the remaining salt-cake consisted of sodium bisulphate and water of crystallisation. The nitric acid produced showed in both cases 1·38 sp. gr. at 21° C.; to produce stronger acid it must be redistilled with concentrated sulphuric acid.

Condensation of Nitric Acid.

The condensation of nitric acid is, properly speaking, only a cooling-process, but it is preferably carried on in such manner that, in the first instance, stronger and weaker acid, coming over at different stages, are separately collected, and that, if possible, the above-mentioned impurities (p. 160) are kept out of the acid and are separately treated. For many years, which now appears strange to us, in this distilling and condensing process only air-cooling was employed, and it is only during recent years that the much more efficient system of water-cooling, which is so universal in other distilling processes, has been applied for nitric acid, and that with complete success.

The old condensing-plant for nitric acid consisted entirely of a series of earthenware receivers (Woulfe's bottles), combined in sets of six to twenty and more, according to the size of the retort. Sometimes two or even more of these jars are superposed over one another, in order to increase the cooling-surface. According to the strength of acid intended to be made, they are either left empty or charged with a little water, as already mentioned. Sometimes they are cooled on the outside with water; but generally this is not the case. Each of the jars is provided with a bottom tap for running off the condensed acid; that from the first two receivers is more impure than that of the others, as it contains a little sulphuric acid and iron carried over from the retort. The acid becomes weaker the further the receivers are from the retort. Since the receivers now and then crack with the heat, it is advisable to put them on stoneware saucers provided with a spout, for collecting the acid running out.

The cement used for joining the receivers with the pipes, etc., has been described on pp. 147 and 149 *Cf.* also the Cellarius receivers, described in our third edition, Vol. II. (1909), p. 364, a modification of which is described in their Ger. P. 232864. These receivers have had great success in the condensation of hydrochloric acid. This style of condensing-plant is still found at many, especially smaller, works; but it must be considered quite out of date, as its cooling action is too imperfect, as the great number of joints is troublesome to keep tight, as the receivers, on breaking, cause great loss and danger to health and life, and as there is always some loss of uncondensed vapours.

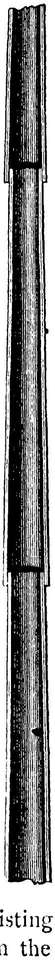


FIG. 26.

A minor improvement which can be made consists in interposing between the retorts and the receivers a somewhat long glass tube, or rather a number of air-cooled glass pipes of slightly conical shape, as shown in Fig. 26, with sufficient fall for the condensed acids not to stop in the tubes and run out of the joints. With a length of from 10 to 13 ft. (the longer the better) the cooling by air is already very efficient. The single tubes are put loosely together, without any cement. Schroeder (Ger. P. 233061) describes a new kind of junction for such pipes.

Gobel proposed (*Dingl. polyt. J.*, ccxx. p. 241), to my knowledge for the first time, the system of cooling such pipes by *water*, employing a long glass tube placed in a trough. This plan must have led to frequent breakages and was probably soon abandoned for that reason, but in principle it was perfectly correct.

Trobridge (B. P. 25435 of 1906) protects earthenware pipes, used in the manufacture of nitric acid, from fracture by cold water in this way: each vertical pipe is surrounded, from the bottom of the condensing tank to near the top, with a lead pipe about an inch wider than the earthenware pipe.

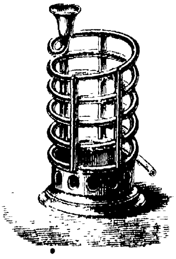


FIG. 27.

Ostwald (Ger. P. 207154) conveys hot nitrogen oxides in pipes made of nickel steel, but care must be taken lest any condensations take place, as nickel steel resists only *gaseous* nitrogen oxides.

A nitric-acid condenser, consisting of sets of perpendicular water-cooled pipes, is described in the B. P. 24332 of 1903, by D. Donnachie (*Chem. Trade J.*, 1904, xxxv. p. 380).

Very efficient are water-cooled *stoneware cooling-worms*, which do away with the necessity of employing a large number of receivers. These coils or worms were first manufactured by Messrs Doulton & Watts, of Lambeth, as shown in Fig. 27, but are now made by many other English and German firms, in various shapes, and are comparatively very durable; good worms stand 300 operations and upwards. They admit of fractionating the products, but are mostly employed when acid of medium strength (up to 82° Tw.) is to be made.

Plate Towers.

Far preferable to coke-towers for both the just-mentioned purposes are the "plate-towers" constructed by the author, in conjunction with L. Rohrmann, and frequently called "Lunge towers." These will be described in detail further on (in Chapter VI.); in this place we will only point out that the use of coke is irrational, because it destroys nitric acid, converting it into nitrous acids and lower oxides. The plate-towers, of which hundreds are in use at nitric-acid works, explosive works, etc., for the above-mentioned purpose, are made of the best fire- and acid-resisting stoneware, and, as will be seen hereafter, they are so constructed as to offer the most intimate possible contact between the gases and liquids. Fig. 28 shows the arrangement as supplied by the Krauschwitzer Thonwaarenfabrik near Muskau, Germany, for the condensation of the last fumes, or the recovery of nitric acid from lower oxides. A B C is the stoneware shell of the tower, D the cover with distributing arrangement, E the plates, F the annular bearers, G drawing-off tap with hydraulic lute, H exit tube, J sight for observing the condensation, K receiver, M injector for drawing air through the neck N, in connection with the last receiver O.

Figs. 29 and 30 show how a cooling-worm can be combined with other pieces to form a complete condensing-apparatus. The vapours, coming from two retorts charged with 6 cwt. of nitrate of soda each, first pass through receivers *a a* for impure acid carried over, which is run off into the carboy *b*, then through the cooling-worms *c c*, discharging their contents of pure acid into carboys *d d*, then into a collecting-receiver *e* and into a "plate-tower" *f* for recovering nitric acid from N_2O_4, and finally into a last receiver *g* and injector *h*. The pots *i i* equally discharging their vapours into *e*, serve for refining (bleaching) the yellow nitric acid (see below).

FIG. 29

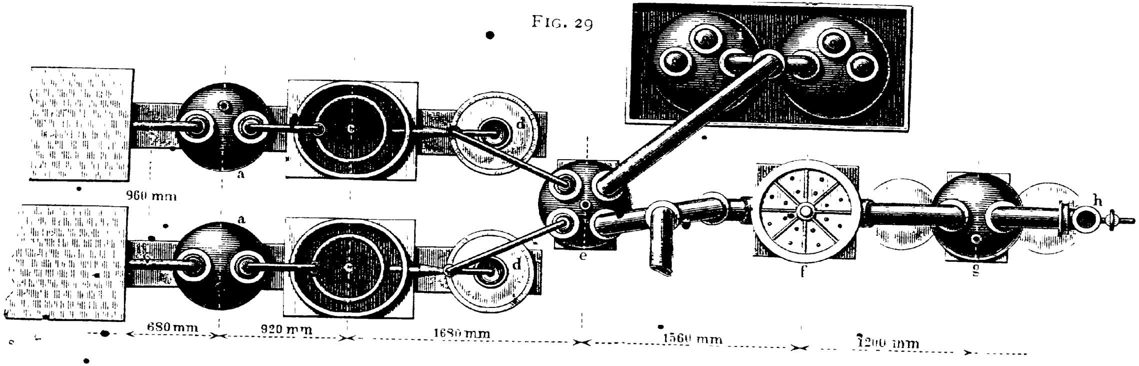
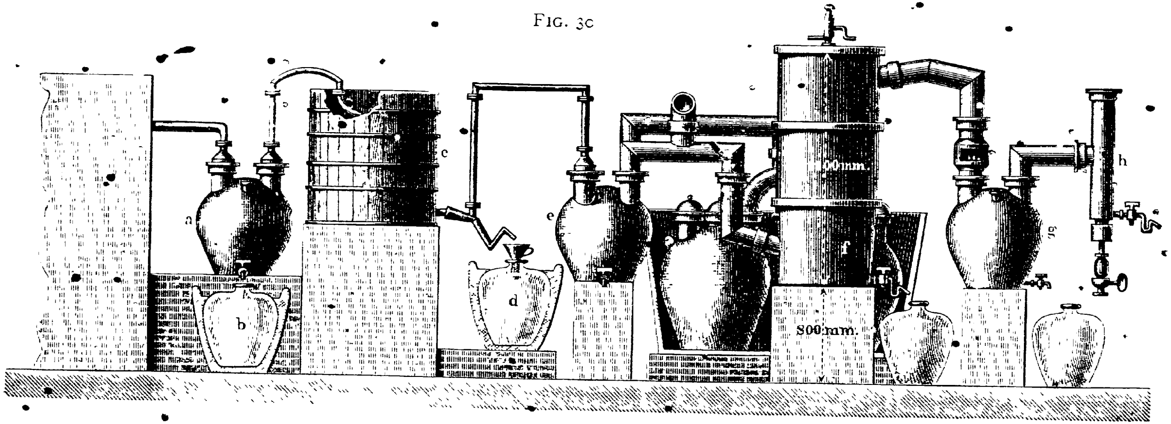

a
a
c
c
d
d
e
f
g
h
960 mm
680 mm
920 mm
1680 mm
1560 mm
1200 mm

FIG. 30


a
b
c
d
e
f
g
h
800 mm.

Such apparatus is especially needed for recovering large quantities of nitrogen oxides, given off in the treatment of waste nitrating acids from the manufacture of nitroglycerine, nitrocellulose, aniline, etc., and reconverting them into nitric acid.

For such purposes it is sometimes necessary to combine several plate-towers in sets, one tower being placed higher than the others and delivering its weak acid to those lower ones, to be got up to strength (Rohrmann and Niedenfuhr, B. P. 29746 of 1897).

The weak acid can also be pumped back to be used over and over again, till it has got up to the maximum strength (1·38 or 1·40 sp.gr.). Figs. 31 and 32 show a complete nitric-acid regeneration plant, with plate-towers, as employed after long experience by H. H. Niedenführ. Pipe *a* (6 in. wide) comes from the denitrator; it is preferably rather long, say 40 ft., so as to cool the gases which pass through receiver *b* into the first tower R_1; glass tube *c* admits of watching the process. R_1 is filled with 34 Lunge plates. The second tower R_2 contains 30 Lunge plates and above them 2 ft. of stoneware balls. The connecting pipe between the towers contains a "Kirchhoff pipe" *d*, which admits of mixing air with the gases in case of need. Pipe *e* takes the gases away from R_2, through the regulating "sight" *f* into receiver *g*, and through *h* into the chimney. V_1, V_2 are cisterns for feeding the towers; V_1 in the beginning receives a little water, V_2 is entirely filled with water. As soon as the denitrator has been started, water is run down from V_1 into R_1 drop by drop, and from V_2 into R_2 in a strong jet, sufficient for absorbing all nitrous products. The liquid from R_2 is collected in V_4, and is pumped back by the "Plath" pump P (to be described later on) into V_1 and V_2. With this weak acid R_1 is later on fed to such an extent that the acid recovered here comes out with the desired strength and runs into V_3. On the other hand, R_2 is always fed up to the extent of completely recovering the last traces of nitric acid. If the weak acid from V_4 does not suffice for that purpose, it is made up with water, preferably at a temperature of 50° C. The acid condensing in receiver *b* is run into V_3 or V_4, according to its strength, that condensing in receiver *g* always into V_1.

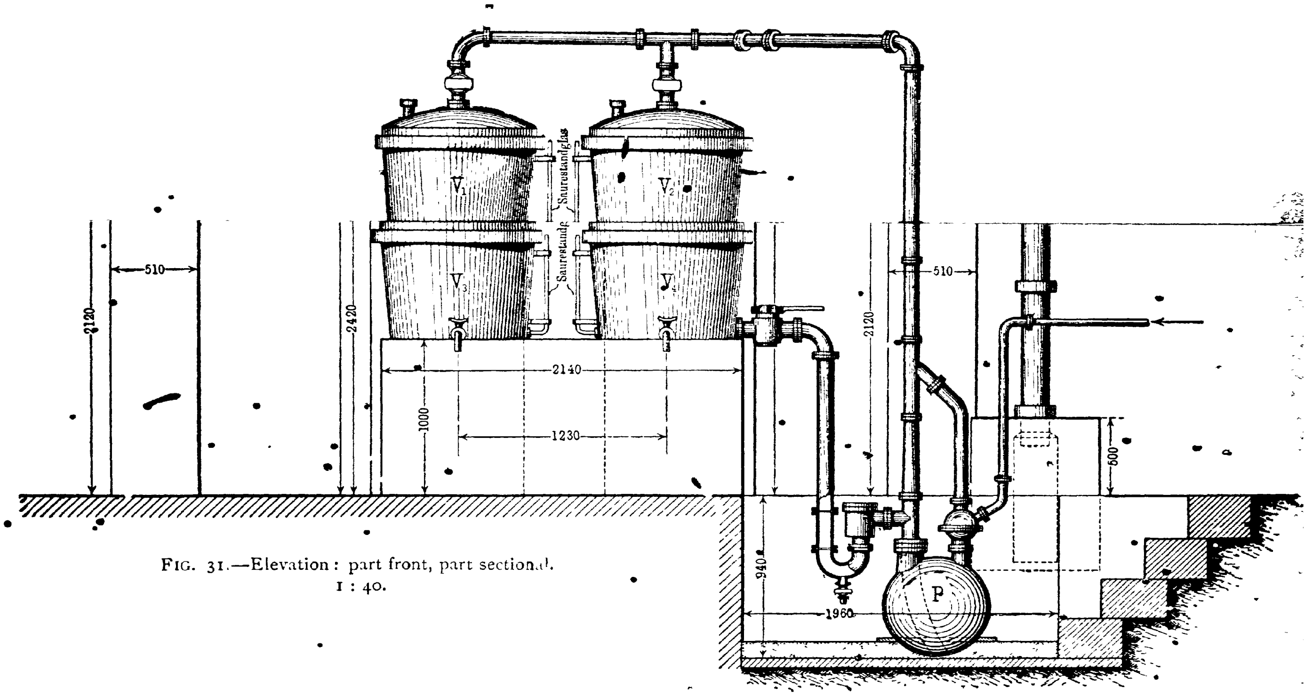


FIG. 31.—Elevation: part front, part sectional.
1 : 40.

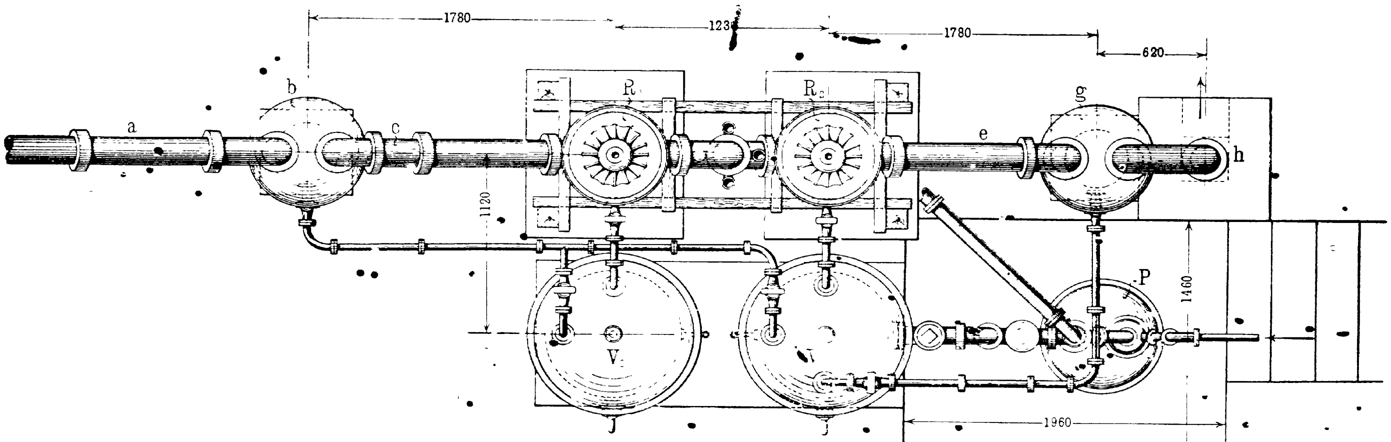


FIG 32.

Refining or Bleaching Nitric Acid.

The *refining* or *bleaching* of nitric acid consists in driving off the lower oxides, so that the acid becomes colourless. This can be done by long heating in a water-bath, which is a tedious operation—much more quickly if a current of air is blown through the gently heated acid; the air together with the gas contained in it is conducted through a small coke-tower, or, preferably, a small "plate-tower" (see p. 164), fed with water, where dilute nitric acid is obtained. This refining is, of course, unnecessary for nitric acid used in the manufacture of sulphuric acid and for many other purposes.

Hirsch (Ger. P. 46096) runs the impure acid through a stoneware worm, placed in water of 80° C. Air is blown in at the bottom, and the feed of nitric acid is so regulated that it runs out at the bottom at a temperature of 60° C and sufficiently bleached. It runs through a second worm placed in cold water, and can then be put into the carboys. The nitrous gases escaping at the top of the first worm are treated in the usual manner. One worm can purify several tons of acid per diem. The same process may also serve for treating the waste acid of nitroglycerine and nitrobenzene works; in this case air heated to 150° C. or steam is blown in at the bottom, and the feed of acid is so regulated that it issues, at a temperature of 140° C., as comparatively pure sulphuric acid.

The French Government gunpowder works have employed such worms for a long time for this purpose. An ordinary size of worm furnishes 2 cwt. sulphuric acid per hour, with less than 0·3 per cent. N_2O_4 and practically free from chlorine.

The *Griesheim process* does away with the necessity of bleaching the nitric acid, as this acid is thereby produced at once in a pure state. (A similar result is aimed at by the apparatus of Guttmann in its recent form and by that of Valentiner, to be described later on.) The Chemische Fabrik Griesheim (Ger. P. 59099) places behind the retort a reflux-cooler, consisting of a Rohrmann stoneware worm contained in a water-tub kept at about 60° C. by the heat of the operation itself. The acid vapours ascending in this cooler are partially condensed there; in consequence of the high temperature the lower nitrogen oxides (together with the chlorine) escape in the state of vapour, and are condensed by air and water in a "Lunge tower" (plate-column) to weak nitric acid. The acid condensing in the worm flows into a receiver, kept at 80° C., and is therefore perfectly pure, no "bleaching" being required. Air is advantageously introduced into the receiver.

This system is illustrated in Fig. 33. We notice that the receiver, into which the acid flows back from the reflux-cooler,

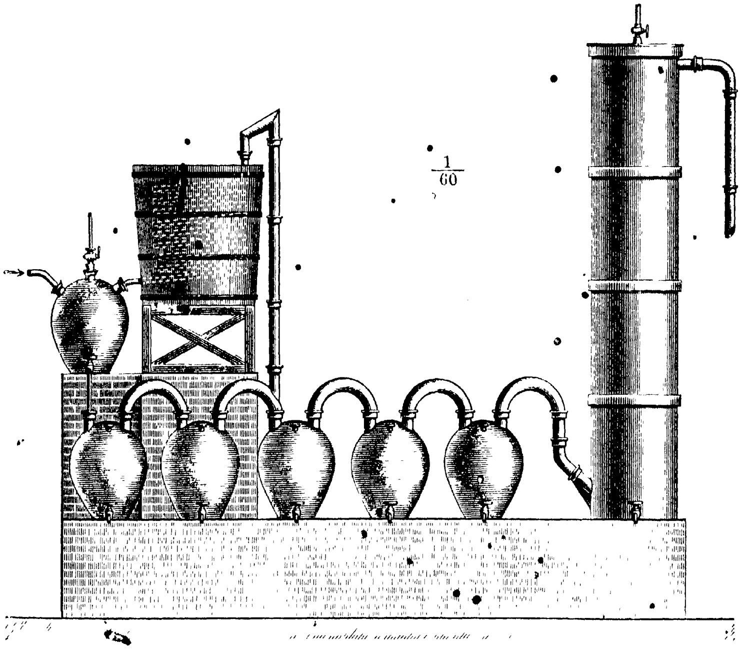


FIG. 33.

is provided with a glass pipe reaching down to the bottom, through which air is introduced, which aids in driving off N_2O_4 and chlorine, etc., and also somewhat cools the acid. The strong and pure acid from this receiver is from time to time run off into a lower receiver, not shown in the figure, where it cools down sufficiently for being withdrawn into carboys; the vapours rising here are also passed into the condensing-apparatus. The vapours issuing from the top of the worm are passed through a few receivers and ultimately into the plate-tower.

In practice the temperature of the water in the worm-tub rises to 40° or 50° C. in the case of slow distillation, and 60° in that of rapid distillation; there is always some fresh water run in, care being taken not to cool too much.

This apparatus is generally combined with the retorts shown on p. 144. Each charge of 400 kl. nitrate of soda (undried) with 450 kl. sulphuric acid (95 per cent. H_2SO_4) yields first 2 litres of impure acid, which is run off separately, then 240 or 250 kl. acid of 48° Baumé = 91 per cent. HNO_3, with less than 1 per cent. N_2O_4, usually only 0·5 per cent. N_2O_4, and no chlorine at all; then 60 or 65 kl. acid of 42° to 44° Baumé, perfectly clear, and 8 kl. of 25° to 30° Baumé impure acid from the tower. When working with dried nitrate, the first 250 kl. of acid show 49° B. = 93 per cent. NHO_3. The weaker acid (42° B.) can be put back into the retort and recovered as strong acid in the next distillation. The nitre-cake tests about 30 per cent. "free" SO_3.

The Griesheim system has been working for many years at a number of factories with perfect satisfaction.

O. Guttmann (B. P. 8915 of 1890) has constructed a nitric-acid condensing-apparatus on the principle of building it up entirely of perpendicular pipes, so arranged that the gases travel upwards and downwards and the acid is run off at the bottom, as it is liquefied, by means of hydraulically sealed branch-pipes, into a common reservoir. The pipes are 8 ft. long and have thin walls (⅓ in. thick), they perform the condensation incomparably better than ordinary receivers, even when merely cooled by air, but in this case there must be a considerable number of such 8-ft. pipes, say fifteen or twenty, to finish off a charge of 12 cwt. in a shift of ten or eleven hours. The last pipe is connected with a "Lunge tower" (plate-tower, *cf.* p. 164), fed with water, in order to retain the uncondensed oxides, in the shape of weak nitric acid, amounting to about 5 to 7 per cent. of the total acid. The Guttmann system is especially suitable for the manufacture of strong nitric acid, of course by means of dried nitrate and strong sulphuric acid.

The former shape of Guttmann's system is shown in our second edition, pp. 890 and 891. Many plants have been

erected on that principle with great success. Later on (Ger. P. 73421), Guttmann improved his system in various ways. He fixed an injector, fed with compressed air, immediately behind the exit-tube from the still, where the whole of the vapours are still uncondensed. They are thus rapidly drawn away from the retort and mixed with hot air. It is contended that in this way nitric acid with not more than 0·7 per cent. N_2O_4 and at a concentration of 97 per cent. can be made during the whole of the process. The acid is as nearly colourless as can be desired. [If all the acid is 97 per cent, what becomes of the water contained in the sulphuric acid, unless this is of equal strength? *Cf.* also Volney, p. 160.]

Another improvement of Guttmann's is the substitution of water-cooling for air-cooling, which admits of a considerable saving in pipes. There are six of these, contained in a water-tank, through the bottom of which they pass water-tight by means of rubber rings. Guttmann states that here all the acid can be obtained with 96 per cent. HNO_3, and slightly over 1 per cent. N_2O_4; this increase of N_2O_4 is caused by the greater rapidity of the cooling, which does not leave so much time for the oxidation of NO_2 by the air. Otherwise the condensing battery is similar to the first, inclusive of the plate-tower.

Another patent of Guttmann's is B. P. 18189 of 1897. In his B. P. 13694 of 1901, he describes an arrangement for condensing nitric acid at a comparatively high temperature, when it is less liable to absorb nitrous gases.

Figs. 34, 35, 36 show a Guttmann plant with improvements, as designed by H. H. Niedenführ and supplied by the Krauschwitz pottery. The drawings are to scale and explain themselves. Each retort, with its set of cooling-pipes, etc., decomposes from 12 to 14 cwt. of nitrate of soda in a working day of twelve or fourteen hours; with somewhat larger retorts, the cooling-battery can be driven up to 20 cwt. nitrate per day.

Bate and Orme, of the National Explosives Co., have patented the following improvements of Guttmann's "water-battery" (B. P. 25790, 24th November 1902). The object is: to ensure more efficient circulation of the condensing water; to enable a defective pipe to be removed and replaced without interfering with the other pipes, and to avoid reducing the strength of the acid if a pipe should crack or leak while the charge is being worked off. Each vertical condensing-pipe, or as many of them as may be necessary, is surrounded by a separate water-jacket, which in case of a crack or leak may be rapidly emptied. The condenser otherwise resembles a Guttmann water-battery, but is claimed to be superior to this in the above-mentioned respects. These water-jackets are made of lead; they are open at the top and are fused to the lead covering of the wooden frame holding the pipes in their places, and they are made to hold water by means of a gland ring and rubber joint ring of circular section. The specification gives all details of the construction of the water-jackets and other parts of the apparatus. It has been successfully at work for some time at the Hayle Explosive works, where the process is as follows:—The vapours issuing from the retorts described on p. 149 pass into an inclined stoneware conduit, with a glass bulb in the middle, and thence into a series of five stoneware pipes, about 5 ft. long and 4 in. wide each, connected alternately at top and bottom. The first three of the set are converted into Liebig coolers by means of open-topped lead-jackets, about 8 in. wide, fed with cold water at the bottom. The last two pipes are left uncovered and are merely cooled by the air. These five pipes communicate at the bottom by a Guttmann "chamber-pipe," or in any other suitable way, with a pipe conveying the condensed strong acid into a closed receiver, placed outside the building. The inlet-pipe is fixed tightly in the receiver and is provided with a side tap through which, during the last stage of the operation, the weaker acid condensed then is run into another receiver. In these vertical pipes the acid-vapours are almost entirely condensed to strong acid. The remainder passes through six ordinary receivers, charged with 6 in. of water, which is left there until the specific gravity amounts to 1·42 or 1·43. Lastly, the gases from four retorts pass into a Lunge tower fed with a little water. By pumping back the weak acid formed here it may be brought to sp. gr. 1·40. All the acid from the six receivers and the weak acid condensing in the pipes towards the end of the operation, which altogether amounts to about 5 per cent. of the total, is put back into the retort in a subsequent operation, so that the *whole* of the acid is eventually obtained of sp. gr. 1·507 = 92 per cent. HNO_3, inclusive of 1 to 1·2 per cent. N_2O_4. This amounts to 97 per cent. of the theoretical quantity. Two per cent. of the nitrate is left undecomposed in the nitre-cake; this admits of conducting the separation in such a manner that the residual nitre-cake retains enough water to obtain all the nitric acid in the strong state, as stated above. It is entirely free from sulphuric acid, chlorine, and iron. The 12 cwt. nitre charged yield 8¾ to 9 cwt. strong nitric acid, no weak acid at all leaving the process. This should be contrasted with the Valentiner process, which in one distillation furnishes only 80 per cent. of the acid in a strong state.

The *fogs* occurring in nitrous gases, especially when these gases come into contact with moisture, and which contain a good deal of N_2O_4, may be precipitated (Ger. P. 233729 of the Badische Anilin- und Sodafabrik) by passing the mixture of gases and fog between sparking and non-sparking electrodes.

Valentiner (B. Ps. 610 of 1892 and 19192 of 1895; Figs. 37 and 38) manufactures nitric acid in a *vacuum*. The retort in which the sodium nitrate is decomposed with sulphuric acid is connected with a cooling-worm, and this is connected with a receiver, from which, with the interposition of a Woulfe's bottle, the air is aspirated by an air-pump. In this way the most highly concentrated pure nitric acid can be obtained. Perfectly pure nitric monohydrate, produced by this process, is now found in commerce. [Before Valentiner (whose patent dates 8th September 1891), I had shown that this can be done by distilling *in vacuo*, *Z. angew. Chem.*, 1891, p. 167, published 15th March 1891.]

Hallwell (*Chem. Zeit.*, 1895, p. 118) gives some details of the practical application of Valentiner's process. The cast-iron retort holds 16 cwt. of nitrate of soda and is nearly globular in form (it is shown in Fig. 19, p. 148). It is not heated directly by the flame, but is surrounded by hot gases. At the top there are necks for the acid vapour, for charging the nitrate, for letting in air, for a thermometer (in a pipe closed at the bottom), and for introducing sulphuric acid. The 8-in. wide neck which carries away the acid vapours is continued into a glass cylinder, through which the inside can be observed, then into an earthenware bend, connected with an earthenware worm of 2½-in. bore and 50 sq. ft. cooling-surface, ending in a three-way cock. Then follow two earthenware receivers of 60 galls. capacity each, with outlet-cocks at the bottom, a receiver of 18 galls., a smaller

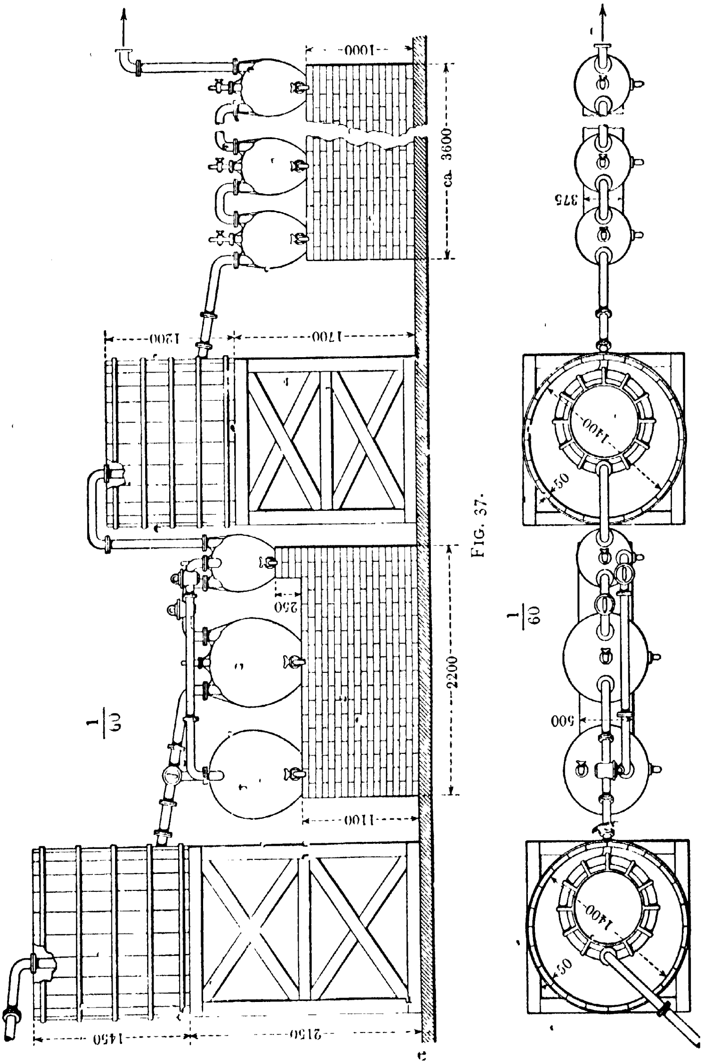

ca 3600
1700
1/60
1/60

FIG. 37.

earthenware worm (2½-in. bore and 25 sq. ft. cooling-surface), a 60-gall. receiver and five 18-gall. receivers, all of which are provided with outlet-cocks at the bottom and air-cocks at the top. The second small receiver behind the second worm is charged with water, the fourth with sulphuric acid; in these the inlet-pipes are deep enough to dip into the liquid. The last receiver is connected with the air-pump. The two large receivers behind the first worm take most of the condensed acid and are alternately put into series by means of the three-way cock; thus the acid can be drawn off without interrupting the work. The joints are all made by means of flanges provided with rills and a cement made of silicate of soda and asbestos (*cf.* p. 149). The vacuum helps to keep the joints tight, and they stand very well.

When the nitrate has been charged, all necks are closed, the air-pump is started, and by opening a tap in the connecting-pipe sulphuric acid is drawn in from a store-tank. Much gas is given off at once; first of all nitrosyl chloride, which mostly travels as far as the receivers behind the second worm. When the vacuum has gone up to 500 mm. of mercury, the fire is started and the thermometer rises to 80°, which temperature is kept up during the principal phase. The vacuum is kept at 650 or 670 mm. In the end the temperature must be raised to 120° or at most 130°. When no more acid distils over, the air-pump is stopped, and the temperature is raised to 170° or 175°, in order to render the nitre-cake more liquid.

By means of this low temperature the decomposition of the nitric acid and the reducing-action of the iron are brought to a minimum. Therefore the yield is almost equal to theory, and that mostly in the shape of strong acid. With undried nitre and sulphuric acid of 142° Tw. the yield, according to Hallwell, is 95·7 per cent. of the theoretical, in the shape of acid of 90½° Tw. (78 per cent. HNO_3), and 3·8 per cent. impure acid of 21½° Tw., together 99·5 per cent. With undried nitrate and sulphuric acid of 160° Tw. the yield is 99 per cent. nitric acid of 93½° Tw. (81 per cent. HNO_3), and 0·8 per cent. as dilute acid, altogether 99·8 per cent. The weak acid is left in the receivers till it has risen to 66° Tw. With dry nitrate and sulphuric acid 168° Tw., real nitric monohydrate can be obtained. The usual strength, 100° Tw., contains only 0·04 per cent. N_2O_3 and no chlorine at all, against 0·95 to 1·92 per cent. N_2O_3 in the ordinary 100° acid.

Hallwell states that while in other processes charges of 6 to 8 cwt. nitrate require from fifteen to twenty hours to be worked off, here a 16 cwt. charge takes only seven or eight hours, and two charges are easily made in twenty-four hours, which means four or five times the usual quantity. The consumption of coal is 8 or 9 parts for firing and 6 or 7 parts for the vacuum, altogether 14 or 16 parts to 100 nitrate, against 32 to 35 parts in the old process. There is also no steam or compressed air needed for refining the acid. The durability of the retorts is greater than in the old process, and the earthenware vessels do not suffer at all. The temperature of the first receivers is only 35° to 42°, the back receivers are cold; they never crack, nor do they collapse through the atmospheric pressure, as they are made rather thick-walled and nearly globular in shape. Any cracks in the pipes or bad places in the receivers are cured by putting on asbestos paper soaked in silicate of soda solution. If too much frothing is observed through the glass cylinder this is at once remedied by opening the air-cock. The total length of the apparatus is only 40 ft., the width of the furnace 17 ft., that of the condensing-plant 5 ft. Large apparatus holding from 50 to 60 cwt. is to be constructed. The sanitary drawbacks of the ordinary nitric acid manufacture are absent when working with a vacuum.

The action of the acid gases escaping from the condensation (especially NOCl) upon the air-pump must be prevented by charging the last receiver with milk of lime, which should, of course, be renewed from time to time.

Further communications on the Valentiner process have been made by Franke (*Chem. Zeit.*, 1897, p. 511). For each ton of nitrate decomposed there should be about 87 cub. ft. condensing-space. The retorts should be entirely surrounded by the fire, or their upper part and the branch-pipe should be protected by an acid-proof lining. With sufficient condensing-space and good cooling, and if the formation of N_2O_4 is prevented, the yield should be almost the theoretical, since only part of the chlorides can escape. The nitre-cake is free from nitrogen compounds, and the first receiver, which is filled with water, is not changed even after several operations. The temperature during the distillation itself is hardly 100° C., but later on it must rise to 175°, to make the nitre-cake sufficiently liquid. The hot vapours then formed may decompose some of the condensed acid, unless they are very well cooled immediately behind the retort. Theoretically 1000 kg. 96 per cent. nitrate of soda, with 2 per cent. water, treated with 1000 kg. 94 per cent. sulphuric acid, should furnish 796·5 kg. nitric acid of sp. gr. 1·486 (89·3 per cent. HNO_3); from 1000 kg. 96 per cent. nitrate, previously dried, 771·5 kg. nitric acid sp. gr. 1·497 (92·2 per cent. HNO_3) should be obtained, and practically the yield need not be much less. But with concentrated acid there is much frothing, through the production of N_2O_4, because the acid does not at once penetrate through the nitrate; this is avoided by employing more sulphuric acid, or by introducing liquid nitric acid into the retort. Valentiner later on recommended the preparation of stronger nitric acid by redistilling the weak acid in the vacuum with concentrated sulphuric acid; but this double distillation costs decidedly more acid, coals, and wages in comparison with the direct distillation. *Cf.* also the same author in *Z. angew. Chem.*, 1899, p. 269. Bergmann (*ibid.*, 1909, p. 1003) also reports favourably on this process, but finds it necessary to pass the gases through milk of lime before they reach the pump, in order to retain the nitrosyl chloride. He consumes 5 cwt. coals for a charge of 16 cwt. nitrate.

The manufacture of nitric acid by means of a vacuum has also been patented by Dreyfus (B. P. 13826 of 1895), who mentions a temperature of 170° to 190°.

In spite of the disadvantage that a double distillation is required in order to obtain very strong nitric acid, the Valentiner system has been introduced in many factories. According to the 40*th Report on Alkali Works*, in the year 1903, 14 units of this system were at work in the 7th district alone (p. 165). This is confirmed in the 41*st Report*, p. 137. Owing to the low temperature, the material of the apparatus is more durable, the product is pure, and the yield almost equal to theory. In the latter respect, as Guttmann remarks, the results in all well-conducted factories are about the same. One hundred parts real $NaNO_3$ ought to yield 74·13 parts real HNO_3; but of course any NO_2 contained in the acid must be deducted from this, and at least 5 per cent. is necessarily obtained as weak acid (tower acid).

The Valentiner system has been represented as decidedly inferior to Guttmann's by some observations made in a scientific publication in 1901, but has been quite as strongly defended from the other side. We can here only give the respective references: *Z. angew. Chem.*, 1901, pp. 413, 495, 571, 658, and 731.

Cf. also Volney's results on the smaller scale when distilling in a vacuum, p. 161.

A modification of the process, by which it is possible to obtain strong acid in the first distillation, consists in replacing about one-third of the ordinary charge of the retorts by nitric acid of sp. gr. 1·425 and then distilling; in this case the nitric acid, corresponding to the sodium nitrate charged is obtained of sp. gr. 1·50, and the weaker acid, put into the retort, is recovered in the same state.

Hart (B. P. 17289 of 1894) uses for the condensation of nitric acid an apparatus consisting of a series of superposed glass tubes, slightly inclined to the horizontal, which starts from an upright stand-pipe and ends in another upright pipe. The pipes are cooled by squirting water upon them or otherwise. The vapours pass simultaneously through all the inclined pipes. As the water squirted on to the glass tubes evaporates, its cooling-action is very strong. Hart asserts that by his method the distillation is effected in half the usual time, with very little fuel and slight formation of N_2O_4. There are fifteen tubes to each condenser, about an inch wide and 6 ft. long, for a retort working off 1000 lb. of sodium nitrate in eight hours. This system has been introduced with great success in a number of American and English works.

Dieterle and Rohrmann (Ger. P. 85240) promote the evolution of gases in the nitric-acid retort by the introduction of some inert gas, which must certainly be an obstacle to condensation. Their object is more rationally attained by the application of a vacuum, as done by Valentiner (see also Guttmann's injectors, p. 171).

Skoglund's condenser for nitric acid (Ger. Ps. 104357 and 105704; Fr. P. 271025; Amer. P. 603402; the patents belong to the Martin Kalbfleisch Co., of New York), according to

A. F. Otto (*Z. f. Schiess u. Sprengwesen*, 1906, p. 325), is employed in many North American factories, especially nitroglycerine and guncotton works. There are also condensers of this kind in two French dynamite works.

E. Wolff (*ibid.*, p. 373) gives a detailed description of it. By this apparatus by a single operation *pure* nitric acid is obtained, which does not require any special treatment in order to remove the lower nitrogen oxides, as it contains only 0·05 to 0·10 per cent. N_2O_3, and its strength is always over 94 per cent., often nearly 95 per cent. The "bleaching" and the removal of the lower nitrogen oxides is effected by the nitric acid vapours themselves, and there is no weak acid going out, since that which is formed in the process at once goes back into it. The apparatus consists of a cast-iron retort, A, Fig. 39, a stoneware "reaction-column," B, packed with an acid-resisting material; a cooling-worm, E, and two columns *C*, *C*, similar to B, in which the vapours of N_2O_3 and NO_2 are removed. The retort A may be of any shape, but it should be sufficiently large for treating 1500 kg. sodium nitrate in one operation; or else two retorts for 750 kg. nitrate each are employed. For 1500 kg. nitrate suffices a cylinder, 3·6 m. long and 1·70 m. diameter; the

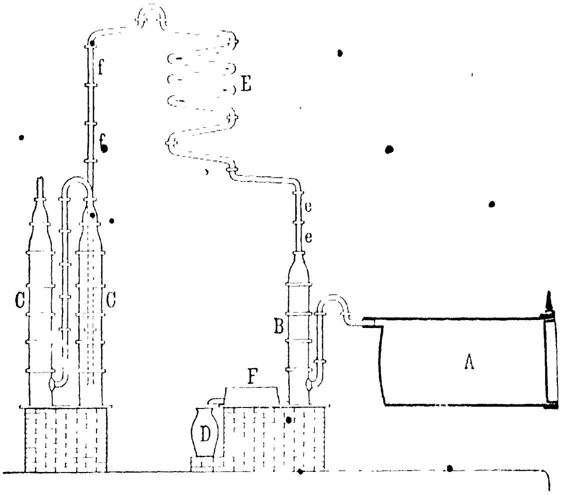


FIG. 39.

average thickness of metal is 4 to 5 cm., the weight about 7 tons. One of its ends is closed at the bottom by a cast-iron block, 36 cm. high and 36 cm. thick, provided with a discharging-hole for the bisulphate. This block is joined to the retort by a cement, composed of 89 parts of cast-iron filings, 4 brimstone, and 7 sal-ammoniac. Above this block the end of the retort is closed by a paste, composed of silica bricks with a mortar consisting of 50 parts fireclay, 25 siliceous sand, and 25 Portland cement. This end-masonry must be built with the greatest care; the bricks must be smooth and evenly cut, placed close together, completely bedded in mortar, and exactly fitted to the sides of the retort. In the upper part of it there is a charging-hole for the nitrate, 50 x 30 cm., closed by a stoneware or cast-iron plate with a hole for running in the sulphuric acid. The reaction-tower B is 40 to 50 cm. wide, and consists of five cylinders, 60 cm. high each. In the middle of the height of the lowest cylinder there is an opening for the entrance of the gases, and at its bottom another for running off the condensing acid. This bottom cylinder is covered by a perforated stoneware plate, on which rest three plain cylinders, and finally the top part, which is cone-shaped in order to be joined with the connecting-pipes *c*, *c*, which are 18 cm. wide. The cylinders are joined by a cement, made of sodium silicate and barium sulphate. This tower is packed with lumps of quartz or other acid-resisting material. The condensing-part E contains, first, a stoneware pipe, and upon this a leaden cooling-worm, 10 cm. wide inside, 1 cm. thickness of lead, and 500 kg. weight, bent as shown in the diagram; at the top it is joined to a stoneware pipe, connecting it with the end-towers C, C, which are similar to B, but higher by two cylinders. The nitric-acid vapours, generated in A, rise through B and the worm E, which is cooled on the outside by water flowing upon it and carried away in tin spouts. The acid condensing here flows back into B; the hot vapours meeting it there, carry away all N_2O_3, N_2O_4, and Cl. When running out of B, the acid passes through a lead pipe, slightly inclined towards the tower, and thus always remaining luted with acid, so that no vapours can escape here. This pipe lies in a lead box F, which receives the water coming down from the coil E, and the acid from here runs into the receiver D. The acid vapours, not condensed in E, are kept back in the towers C, C. The first of these is fed with strong sulphuric acid (94 per cent. H_2SO_4), which flows upon a star-shaped lead plate in the top part and, as it flows out, is pumped back upon the second tower C. A slight feed of such acid suffices for keeping back the nitrous and nitric vapours, and this acid comes out at the bottom, about 200 kg. during each working of a charge, testing about 25 per cent. HNO_3, inclusive of 8 to 10 per cent. in the shape of N_2O_3. This acid mixture may be used up in the Glover tower of a sulphuric-acid factory, or denitrated in the way it is done at nitroglycerine factories, or re-employed as part of the acid needed for the cylinder A of the Skoglund apparatus.

The following is a description of the operation of this apparatus. After closing the hole for running off the bisulphate, the retort A is charged with 1450 kg. nitrate of soda, such as it comes out of the warehouse, containing about 2 per cent. moisture. It is an additional advantage of this system that the nitre need not be previously dried. The nitrate is spread out equally, the closing-plate is put in, and the sulphuric acid is run in. For each operation 1535 kg. sulphuric acid of 95·5 to 96 per cent. is taken, and to this is added the whole of the weak nitric acid (about 44° B.) obtained in the previous operation. As a matter of course, somewhat more and stronger sulphuric acid is required than in the old system, on account of the moisture of the nitrate and the water contained in the weak nitric acid. Now the fire is lighted underneath the retort; if this had cooled down altogether, the distillation commences after one and a half or two hours, as is recognised by the smell of chlorine. From this moment the fire on the grate must be kept low and very equal on the grate. Water is now run over the coil E, and sulphuric acid into the towers C, C. The nitric acid flowing out of B into D shows at first 40° B. and gradually rises to 47° B. At this point about 50 kg. has run out. The strength now rises to 48·5° to 49° B., and again goes down to 47° B.; from this point the acid is again kept separate and is mixed with the weaker acid condensed before. The "strong" acid, between 47° and 49° B., shows on an average 48·3° B., 94 to 95 per cent. HNO_3, and less than 0·10 per cent. N_2O_3; it is of a light green colour and gives off *no* red vapours of N_2O_4. The "weak" acid, that below 48° B., is separately collected in a stoneware tank. When the strength of the acid has gone down to 36° B., the distillation is interrupted, the bisulphate is run off, and a fresh operation may be made after three hours. It is important not to go below 36° B.; there is very little acid gained thereby, and this weak acid acts strongly on the lead of the cooling-worm. The distillation of the "strong" acid lasts seventeen to fifteen hours, that of the "weak" acid four to six hours, so that an operation can be made every day.

The yield from the above-stated charge is: 1000 kg. strong nitric acid of 94 to 95 per cent. HNO_3 and less than 0·10 per cent. N_2O_3; 250 kg. "weak" nitric acid and 200 kg. of the mixed sulphuric and nitric acid. The lead cooler lasts a very long time without repairs, as it is soon coated inside with a protecting layer of lead nitrate; it stands upwards of 100 charges, without any repairs, except renewing the last 40 or 50 cm. of piping, connected with the lowest stoneware pipe. But this lead worm must be always kept wetted outside with cold water.

The average yield from this process for 100 kg. monohydrate is: strong acid 91·50, weak acid 0·75, acid mixture 4·75,[1] loss 3 per cent. This should be compared with the fact that in other processes from 100 monohydrate only 80 per cent. strong acid is obtained.

Guttmann (*Z. f. Schief. u. Sprengwesen*, 1906, p. 376) gives figures to show that the results of that process are not as good as those obtained by his own apparatus, described *suprà*, pp. 171 *et seq.*

Treatment of the Lower Nitrogen Oxides, formed in the Manufacture of Nitric Acid.

As far as this subject belongs to the synthetical production of nitric acid from elementary nitrogen or from ammonia, it will be dealt with later on, in connection with that subject. In the present instance we describe only such methods for the above-stated purpose as are primarily intended for the ordinary manufacture of nitric acid, and as have not been already previously mentioned in connection with the condensation of nitric acid.

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[1] This statement does not agree with the figures given at an earlier place of this paper.

The primary object is, of course, to convert these lower oxides, NO, N_2O_3, and NO_2 or N_2O_4 (nitrogen protoxide, N_2O, is of course out of the question), into nitric acid, HNO_3, as far as it is at all possible; but at all events they must be brought into a form in which they do not escape into the air as "noxious vapours." This is most simply but not most advantageously accomplished by employing a small "Gay-Lussac tower," consisting of a stack of stoneware pipes filled with coke and continually fed with sulphuric acid of 144° to 152° Tw. The gas enters at the bottom and issues at the top, and thereby gives up all its nitrous and hyponitric acid to the sulphuric acid which arrives at the bottom as a more or less rich "nitrous vitriol," and can be employed in the manufacture of sulphuric acid. For a ton of nitre from 3½ to 4 cwt. of sulphuric acid of the above strength are required; and nitrogen acids corresponding to 3 to 5 per cent. of nitric acid of 1·33 sp. gr. are absorbed by the same, more or less, according to the percentage of chlorides in the nitre.

In such manufactures of nitric acid as are not in connection with sulphuric-acid works, the coke-tower can be fed with water. If care is taken that an excess of air is always present, not merely the last remnant of nitric acid is condensed, but the lower nitrogen oxides are likewise converted into nitric acid and thus saved.

We first quote some laboratory investigations on the conversion of the lower nitrogen oxides into nitric acid, and then pass over to the processes employed or proposed for a manufacturing scale.

Lunge and Berl (*Chem. Zeit.*, 1904, p. 1243) showed that the proportion of nitrous and nitric acid in the oxidation of NO by air are not influenced by the dilution of the oxygen, but by the quantity of water and the intensity of agitation. If the mixture of NO and air is at once agitated with a large quantity of water, the NO_2 first formed dissolves as a mixture of nitrous and nitric acid, whose complete conversion into HNO_3 by excess of oxygen takes place very slowly, all the more so the greater the dilution with water. With appropriate quantities of water, the formation of HNO_3 takes place quantitatively.

The combination of nitric oxide and oxygen to nitrogen peroxide does not always take place quite smoothly. Mandl and Russ (*Z. angew. Chem.*, 1908, pp. 486-491) found that the reaction may stop before the stage of N_2O_4 is reached, and that this depends upon the source of the oxygen employed. With compressed oxygen prepared from air it goes on to the end, but not with oxygen obtained from BaO_2, $H_2Cr_2O_7$, and H_2SO_4. With oxygen obtained by the electrolysis of water the formation of N_2O_4 was almost complete, if the O had been passed over heated palladium asbestos, but not otherwise. It appears that the presence of ozone causes the stoppage of the reaction. Possibly perfectly pure NO and O combine very slowly, and their rapid combination requires a catalyser which is consumed by ozone or H_2O_2. Their results are contradicted by Holwech (*ibid.*, pp. 2131-2135), who found that the reaction: $2NO+O_2=N_2O_4$, proceeds completely and with about the same velocity, whether the oxygen was Linde's or ozonised, or made from BaO_2, or from $KCrO_4$.

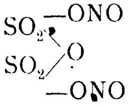
Foerster and Koch (*Z. angew. Chem.*, 1908, pp. 2161-2172) describe their experiments on the action of mixtures of NO_2 and O or air, in different proportions, on water, and on the oxidation of NO_2 by means of ozone, with a view of obtaining nitric acid of higher strength than is otherwise possible. If a mixture obtained from 1 vol. NO+2 vol. O is passed into water, HNO_3 is rapidly formed, until nitric acid of 40 per cent. is obtained. The absorption of NO_2 then slackens gradually, until the nitric acid exceeds 50 per cent., and then goes on more rapidly again. At the ordinary temperature no higher concentration than 68 to 69 per cent. can be obtained; at higher temperatures this goes on more slowly. The highest concentration to be obtained from the interaction of NO_2, O, and H_2O is of approximately the same composition as the mixture of nitric acid and water of minimum vapour pressure. From NO and air with 1 per cent. NO about 40 per cent. nitric acid, with 2 per cent. NO about 52 per cent., with 5 per cent. NO, acid of 55 per cent. can be obtained. The nitrous acid formed primarily decomposes completely in the course of time into nitric acid and NO, which in course of time is oxidised into NO_2. By ozone NO_2 is rapidly oxidised into nitric anhydride, even when mixed with large proportions of air, and by passing the resulting gas-mixture into water or aqueous nitric acid, acid of more than 80 per cent. is easily obtained.

A continuation of this work by Foerster and Blich (*Z. angew.*

Chem., 1910, pp. 2018 *et seq.*) showed that the oxidation of NO by free O to NO_2 between 0° and 100° goes on more rapidly at lower than at higher temperatures, probably because at first some unstable primary oxides are formed. N_2O_3, or mixtures of NO and NO_2, are much better retained by alkaline absorbents than pure NO_2.

Niedenfuhr (Ger. P. 155095), in order to obtain the nitric acid free from the lower nitrogen oxides, condenses it at a high temperature and with application of draught. The fan serving as draught producer is placed behind the condensing-receivers, and in front of the apparatus for oxidising and condensing the lower nitrogen oxides. Thus there is a slight lowering of pressure in the first condensers, by which the nitric acid is obtained in a purer state, and a rather higher pressure in the last part, which favours the oxidation going on there. Between the first condensers and the draught apparatus a cooler is interposed by which the draught apparatus is better protected against the action of the acid gases, and which also facilitates keeping the oxidising apparatus at a low temperature. His B. P. 4353 of 1905 describes the same process, and also a modification by which the conversion of the lower oxides of nitrogen into nitric acid is effected in two plate-towers (p. 164), the first of which is rinsed only moderately so as to produce an acid of high strength, while the second tower is strongly rinsed, without regard to the strength of the acid obtained, which acid may be employed for rinsing the first tower.

In his Ger. P. 160709 Guttmann shows an arrangement for the automatic introduction of air into the gases evolved in the distillation of nitric acid. A conical pipe is put over the gas conduit. At its bottom there are openings for the air (which can be closed); the other end is kept at a certain distance from the gas-pipe, and through the annular space thus formed air is introduced into the gaseous current without the employment of pumps or injectors.

Halvorsen (Norw. P. 15021) exposes very dilute nitrous gases to SO_2 in such manner that nitrosulphonic acid, $SO_2\begin{smallmatrix}-OH\\-OHNO\end{smallmatrix}$, or its anhydride:  are obtained. This compound can be fused in metal vessels in order to make its carriage easier; or else it is dissolved in concentrated sulphuric acid and sent out in metal vessels. The concentrated nitrous vapours are afterwards transformed in towers by means of air and water into nitric acid. Another advantage claimed is that the absorbing apparatus can be made of metal, in lieu of stoneware.

The Norske Aktieselskabet for Elektrokesmisk Industri and Halvorsen (Fr. P. 380190) absorb dilute nitrous gases by lime, or by finely divided salts which are easily decomposable, and kept in constant motion by revolving drums.

Sinding-Larsen (Norw. P. 16083) utilises nitrous gases or dilute nitric acid by means of dolomite. He treats this with the dilute acid in such manner that only the $CaCO_3$ is dissolved and the $MgCO_3$ remains behind. The solution of calcium nitrate is removed by filtration, and the $MgCO_3$ converted into nitrate by means of strong nitric acid. When heating the $Mg(NO_3)_2$ in a current of CO_2, strong HNO_3 distils off and *magnesia usta* is obtained as a by-product.

Naville, P. A. Guye, and C. E. Guye (Fr. P. 385569) convert NO into HNO_3 preferably by alternate, instead of by simultaneous treatment with O and water. The gases are subjected to three successive processes: (1) absorption of two-thirds of the combined N by water, according to the equation $3N_2O_4+2H_2O=4HNO_3+2NO$; (2) desiccation of the residual gas by treatment with anhydrous calcium nitrate or other drying agent, or by refrigeration; (3) oxidisation of NO to N_2O_4 by spontaneous reaction with the excess of oxygen, or by increase of temperature or pressure, or by use of a catalyser. Oxides of N present in air to the extent of only 1 per cent. may be almost completely recovered by five repetitions of such treatment, but in each succeeding stage the reactions are slower and the gases should therefore be retained in the apparatus for a longer period. In any part of the apparatus the pressure may, if desired, be maintained above that of the atmosphere.

The same inventors (Ger. P. 225153; Fr. P. 385605) say that, when the higher oxides of N have been absorbed by sulphuric acid, N_2O_3 is absorbed without formation of HNO_3. Hence the residual gas containing NO should be removed to an oxidising-chamber, in order to convert as completely as possible the NO into N_2O_4, which is then made to react with sulphuric acid again. They employ a series of towers and chambers, so that short periods of absorption alternate with periods of oxidation, the acid being pumped from the bottom of one tower to the top of the next, and finally passed through a heater in which the free nitric acid is distilled off, any oxides of nitrogen produced being returned into the system. The humidity of the gas is so regulated, by preliminary addition of water or by exsiccation, that the moisture just corresponds to the amount of N recoverable as HNO_3, *i.e.*, 1 g. mol. of H_2O for every 2 g. atoms of combined N. In this way, after distilling off the nitric acid, the residual acid is again ready for use as an absorbent. Oxidation is effected either by raising the temperature (not above 200°), or by use of a catalyser, or by compression, and an increased pressure is preferably maintained in the whole system. In practice, a series comprising three absorbers and three oxidisers is found sufficient to almost completely remove oxides of nitrogen from air containing them in small quantities.

The Norske Kvälstofkompagni (E. P. 6265 of 1905) absorbs nitrous gases first by water or dilute nitric acid, and the remaining portion of the gases by dilute alkali or alkali carbonates.

Victinghoff-Scheel (Ger. P. 225706) makes nitric acid from N_2O_4, H_2O, and O by compressing the mixture to 5 to 10 atmospheres. There should be 0·220 kg. water employed for 1 kg. N_2O_4, whereby nitric acid of 98 per cent. is formed.

The Elektrochemische Werke (Fr. P. 388305) concentrate oxides of nitrogen, when mixed with much air, by submitting them to the action of the oxides of Zn, Cu, Mg, or Pb, which furnish nitrates and nitrites, readily decomposed by heat in iron retorts at 500°, or under reduced pressure at lower temperatures.

Scherfenberg and Prager (Ger. P. 202560) place a series of reflux-coolers immediately on the top of the condensing-tower, in which tower the gases are converted into a spray, so that this spray comes into intimate contact with the acid flowing down from the coolers. The coolers consist of a bundle of perpendicular pipes, which are less liable to breakages and leakages than serpentine coolers.

The Salpetersäure-Industrie-Gesellschaft Gelsenkirchen (Ger. P. 237684) introduces the drying agent (sulphuric acid cooled below 180°) into the gases at a temperature at least equal to that of the escaping gases and vapours, and conducts the cooling in such manner that the temperature of the drying agent is in no case considerably higher than that of the gases and vapours in contact with it. Thus, *e.g.*, nitric acid vapours containing 40 to 50 per cent. aqueous vapour are passed into a vertical tube, packed with acid-proof material and cased in a jacket into which cooling-water enters at the bottom; the gases and vapours from the inner tube pass away at the top into a condenser, in which they are further cooled by sulphuric acid, which is thus heated to the temperature of the vapours and injected into the tube at the top. Their Ger. P. 211919 prescribes separating the compounds by superheating above the boiling-point of the highest boiling component, and introducing them into a rectifying column, fed with the lowest-boiling component, so that pure vapour of this component escapes. The Fr. P. is 422902; the Amer. P. (with Pauling), 993868.

Bergius (Ger. P. appl. B. 53617) obtains from mixtures of gaseous nitrogen peroxide with gases containing oxygen and water, concentrated nitric acid, by causing the reaction to take place at higher temperatures and at high pressure which prevents the re-decomposition.

Frederich (B. P. 319 and 403 of 1911) obtains red fuming nitric acid by adding one molecular proportion of water, a little at a time, to one molecular proportion of liquid N_2O_4, contained in an autoclave provided with a stirrer, and introduces oxygen under a pressure of 3 to 5 atmospheres, until the gas is no longer absorbed. Or else nitrogen peroxide is absorbed in wood charcoal, instead of employing liquid N_2O_4, stirring the mixture in an autoclave and introducing oxygen under a pressure of 1·5 to 3 kg. per sq. cm.

The Norske Aktieselskab. and Halvorsen (Fr. P. 363157; Amer. P. 892516; B. P. 3680 of 1906) dissolve nitrosulphonic acid in concentrated sulphuric acid, add a little water and an oxidiser, such as MnO_2, PbO_2, CrO_3, or a chromate, distil off the nitric acid formed in iron retorts, and recover the oxidiser from the residue by electrolysis, thus:

$$Cr_2(SO_4)_3 + 6H_2O = 2CrO_3 + 3H_2SO_4 + 3H_2.$$

The Farbwerke Hochst (B. P. 19032 of 1911), in the process of manufacturing nitric acid from the oxides of nitrogen and oxygen in presence of water, obtain the gas pressure in the apparatus for conveying the liquid into the absorption system by means of oxygen instead of air, and afterwards introduce this oxygen, carrying with it any entrained nitrous gases or vapours, into the absorption system.

Engels and Dürre (Ger. P. 229096) make concentrated nitric acid from concentrated nitrous gases, air, and water, by gradually admitting air in less than the theoretically necessary quantity (except at the close). Thus, *e.g.*, from gases rich in NO_2, such as are formed in the manufacture of oxalic acid from sugar and nitric acid, nitric acid of 60 to 65 per cent. HNO_3 is obtained. The process does not apply to gases containing less than 50 per cent. pure nitrogen oxides.

The Salpetersaure-Industrie-Gesellschaft Gelsenkirchen and Pauling (B. P. 9884 of 1910) cause a current of air containing oxides of nitrogen to meet an opposing current of alkaline liquor, *e.g.* in a series of towers. After the alkali has passed some of the towers, some of the nitrite formed is separated by evaporation of the lye; after it has passed through the rest of the system, nitrate is crystallised from the liquor.

Guye (Fr. P. 404630) treats gases containing N_2O_3 and NO_2 with organic solvents, such as chloroform, carbon tetrachloride, ethyl bromide, chloro- and bromo-benzene, a solution of nitronaphthalene in nitrobenzene, etc., and recovers the gases from the solvent in a concentrated form by distillation or crystallisation of the solvent. Before absorption, the gases are dried by sulphuric acid charged with nitrous fumes, in order that metal apparatus may be employed. Solvents of low boiling-points are unsuitable, if the oxides of nitrogen are diluted with much air.

Vergé (Fr. P. 409194) obtains an improved yield of nitrogen oxides in the synthetic process by the immediate and extreme cooling of the products by means of liquid air. The central zone is brought by the arc to a temperature of 2500°, while the outer part of the reaction chamber is at −200°. The liquid air also removes the NO at once by absorbing and precipitating it in the solid form. The solid oxides may be filtered off and treated with water and air, to obtain nitric acid of any desired strength.

Halvorsen and the Norsk-Hydroelektrisk-Kvaelstof A. S. (Amer. P. 948726; Fr. P. 380490) absorb the fumes by lime or salts of acids which are liberated by nitric acid, suspended in water and kept continually in motion.

Sparre (Amer. P. 1008383, transferred to the Du Pont de Nemours Powder Co.) passes an electric current through a solution of nitrogen oxides and through water, the current density being kept high in the solution of nitrogen oxides, viz., above 100 amp. per square decimetre, but low at the electrode placed in water.

The Badische Anilin- und Sodafabrik recover nitrogen peroxide from gaseous mixtures containing but little of it, in a solid form by the cooling action, produced by compressing the gases, removing the heat produced by compression and adiabatic expansion.

The following patents for the treatment of gases and vapours seem to be especially adapted for the purpose in question: Moscicki, Ger. P. 234259; Maschinenfabrik Buckau, Ger. P. 234509.

Concentration of Nitric Acid.

We have had to speak of this operation incidentally before, *e.g.* in connection with Valentiner's process, pp. 173 *et seq.*

Colin (Fr. P. 211045) prepares fuming nitric acid of sp. gr. 1·5 by distilling nitric acid of 1·4 with sulphuric acid of 1·84 in enamelled cast-iron retorts, and employing a glass three-way cock for separating the distillates.

Erouard (Ger. P. 62714) also concentrates dilute nitric acid, or waste acids from nitrating processes, by adding strong sulphuric acid, or a solution of $CaCl_2$ or $MgCl_2$ [!], and distilling the mixture in a vessel in which it travels in a zigzag direction.

H. A. Frasch (Ger. P. 82578) prepares highly concentrated nitric acid by passing the vapours from the nitric-acid retort through a tower heated above the boiling-point of the acid, in which hot concentrated sulphuric acid is descending, or in which other dehydrating substances, such as anhydrous sulphate of soda or burnt plaster-of-Paris, act upon the mixed vapours.

The Verein Chemischer Fabriken in Mannheim (Ger. P. 85042) places between the still and the condenser, a dephlegmator, from which the dilute acid condensed there runs back into the still. This dephlegmator is kept at a temperature of 85° C., so that the concentrated acid can pass on.

Waldbauer (Ger. P. 155006), in order to avoid the expensive vessels used for distilling crude nitric acid, made of glass, porcelain, or platinum, or of running the impure acid into hot sulphuric acid (whereby the vessels are gradually attacked), fills the stills with some granular material, such as sand, pebbles, broken glass or china, preferably placing fine sand next to the sides of the vessel, then coarse sand and in the centre pebbles. The acid is run upon the latter, gradually flows into the hotter parts near the sides, and is evaporated before it reaches the walls of the still. This process admits of employing stills made of a cheap and durable material, which could not be employed if the acid came into direct contact with it.

Collet (Norw. P. 13925; *Chem. Zeit.*, 1905, p. 457; Amer. P. 854928; Fr. P. 357221) concentrates nitric acid by means of hot air. The escaping gases and vapours are passed through a column fed with dilute nitric acid, then through a cooling-shaft and at last through a vessel filled with lumps of calcium oxide. By this method it is claimed that 60 per cent. nitric acid is made more cheaply than by any other method.

Dieffenbach (Ger. P. 174736; Fr. P. 371688) also concentrates dilute nitric acid by heating it with alkaline polysulphates which take up the water, from which they can be again separated by heating by themselves. This may be done in cast-iron vessels without any visible damage to them. If 100 g. nitric acid of 36° B. is heated with 1000 g. polysulphate of the composition: $NaHSO_4$, H_2SO_4 to 105° to 120°, nearly all the nitric acid distils off with 95 per cent. HNO_3, and the remaining polysulphate is easily concentrated again.

Boeters and Wolffenstein (Ger. Ps. 189865 and 191912) heat nitric acid of, say, 68 per cent., in an iron retort and pass the vapours through a series of stoneware receivers, kept at about 100° by a water- or sand-bath, which are charged with a dehydrated nitrate. When this has taken up enough water the receiver in question is put out of series by means of a three-way tap and is connected with a vacuum, whereby the nitrate is dehydrated and made again fit for use.

The same inventors (Fr. P. 371797) concentrate nitric acid by pouring it over calcium nitrate, dehydrated at 150° to 200° which thereby passes over into a porous mass. Preferably, a counter-current is employed, if necessary with admission of air

For the concentration up to acid of 63 per cent. 1·25 to 1·5 parts of $Ca(NO_3)_2$ is required.

The Chemische Fabrik Griesheim-Elektron (Ger. P. 174736; Amer. P. 819262; Fr. P. 358373, etc.; Johnson's B. P. 19989 of 1905) mix dilute nitric acid at 110° to 130° with polysulphate, distil the concentrated acid off and then raise the temperature to 250° to 300°, whereby the polysulphate is dehydrated and can be used over again after cooling down to 120° to 130°. (This process is not at work now on a commercial scale.)

Uebel (Ger. P. 210803) performs the concentration in stages. First he distils the dilute nitric acid at higher temperatures with sulphuric acid of medium concentration, and treats the distillate with stronger sulphuric acid at lower temperatures; the sulphuric acid used in the second stage is afterwards employed for the first; it is employed at a strength of 80 per cent., to the extent of three times the quantity of the nitric acid. From the second still the nitric acid comes out with 70 to 75 per cent. HNO_3; it runs into the first still, and here a vapour of 90 per cent. comes out, which by partial cooling can be made to yield acid of 95 to 98 per cent. HNO_3. In this way also the waste acid mixtures from nitrating processes may be utilised.

Vietinghoff-Scheel (Ger. P. appl. V8284; later on withdrawn) concentrates the acid by first converting it into ammonium nitrate, drying this and distilling it with concentrated sulphuric acid.

Plath (B. P. 9133 of 1901) makes clear concentrated nitric acid by interposing between the perpendicular cooling-pipes and the receiving-vessel a cooling-worm about 80 ft. long, air being passed through opposite to the current of acid, and the temperature in the cooling-tub being regulated in such a manner that the acid comes out both cold and free from lower nitrogen oxides.

From a private letter I gather the information that the *strongest* ordinary nitric acid, say 96 per cent., cannot be obtained even with dried nitrate and sulphuric monohydrate, unless the retorts are worked at the least possible heat, owing to the strong dissociation of the nitric acid setting in at 86°.

Brauer (Ger. P. 222680; Amer. P. 1008690; B. P. 14381 of 1910) concentrates nitric acid by heating with phosphoric or arsenic acid. These acids have the advantage that they do not, like sulphuric acid, form a chemical combination with nitric acid; hence the heating need not be driven higher than the boiling-point of the nitric acid, which means a saving of fuel and the avoiding of losses by the splitting off of lower nitrogen oxides.

The Swedish Nitric Syndicate (B. P. 10592 of 1908; Ger. Ps. 233031 and 236341; Fr. Ps. 402078 and 402079; Amer. Ps. of Sohlmann, 1009196 and 1009197) concentrate weak nitric acid, especially that obtained by the oxidation of atmospheric nitrogen, by distilling with sulphuric acid in a continuous manner, the acids flowing down in a column heated externally, while a current of hot air (of which but little is required) passes upwards in the column. Or else the concentration is effected in two steps: (1) to about 60 per cent. by direct contact with the gases from the electric furnaces; (2) to 90 to 97 per cent. by distilling with strong sulphuric acid, as above described. The waste heat from the furnace gases is utilised in various ways.

Pauling (B. P. 22037 of 1909) heats dilute nitric acid to a temperature at which it is decomposed into a mixture of NO_2, O, and H_2O, and rapidly cools the products. Thus a mixture of NO_2 and O, nearly free from water, is obtained, from which concentrated nitric acid is readily prepared. His B. P. 22320 of 1910 describes the concentration of nitric acid by causing it to trickle down in a vertical column, together with sulphuric acid, in an ascending stream of steam or hot gases. B. P. 22322 of 1910 describes a modification of this process. His Amer. P. 993868 describes dehydrating nitric acid vapours by passing against a counter-current of sulphuric acid, kept at a temperature near that of the vapours at all stages of the process.

Nathan, J. M. Thomson, and W. T. Thomson (Fr. P. 406806) condense nitric acid vapours by passing them through cooling-worms from the bottom upwards, the cooling being effected by running water on to the top of the coils. The upper ends of these are connected with a vacuum. The nitric acid running out at the bottom is almost free of lower nitrogen oxides.

The Salpetersäure-Industrie-Gesellschaft (Austr. P. appl. A2969) treat nitric-acid vapours by water-absorbing fluids at such temperatures which at least equal those of the vapours going out, and are not essentially higher than this.

Dieffenbach and Uebel (Ger. P. 238370) concentrate nitric acid by distilling it over pyro- or metaphosphoric or the analogous arsenic acids, or acid salts of these, in vessels made of quartz. *E.g.* on heating aqueous nitric acid with pyrophosphoric acid at 110° to 115°, nitric acid of 99 per cent. distils over. The orthophosphoric acid remaining behind is reconverted into pyrophosphoric acid by heating to about 210°.

Hale and Scott (B. Ps. 24379 and 25386 of 1910) cause dilute nitric acid to be absorbed in kieselguhr and heat this in an earthenware or cast-iron retort, if necessary provided with a stirring arrangement, under reduced pressure. The vapours are condensed, and acid of any desired strength may be produced by adjusting the temperature of distillation and the degree of vacuum.

The Farbwerke Höchst (Fr. P. 432990) concentrate nitric acid of 60 or 62 per cent. to a higher point by passing a mixture of nitrogen peroxide and oxygen through it.

The *Soc. anon. le Nitrogène* (Austr P. appl. A133) produce nitric acid upwards of 95 per cent. HNO_3 by treating a mixture of liquid nitrogen peroxide, water, and oxygen in molecular proportions under high pressure.

Other processes for the concentration of nitric acid, apart from those incidentally mentioned *suprà* in various places, will be described *infrà* in connection with the synthetic production of nitric acid from free nitrogen or ammonia.

Manufacture of 100-per-cent. Nitric Acid.—According to Valentiner and Schwarz (Ger. P. 144633) the reason why pure 100-per-cent. nitric acid up to that time had not been obtained in one operation was the difficulty of decomposing sodium nitrate by sulphuric acid of 170° Tw. in the vacuum on a manufacturing scale, owing to the formation of enormous quantities of froth towards the middle of the operation, which is perilous for the stoneware parts of the apparatus and contaminates the distilling acid with bisulphate carried over. This frothing can be avoided by adding the sulphuric acid not all at a time. The retort is charged with the nitrate and with about one-third of the sulphuric acid (170° Tw.) required for complete decomposition; this quantity is completely mechanically absorbed by the nitre. The evolution of nitric acid commences immediately, and when the boiling temperature has been attained, the nitric acid begins to distil off quietly and evenly. According to the progress of distillation, fresh sulphuric acid is run into the retort, at such a rate that there is always enough sulphuric acid present to decompose the nitrate into bisulphate and nitric acid. The sulphuric acid is run into the retort neck through a vessel, filled with pumice blocks, through which the nitric-acid vapours must pass before leaving the retort, by which process they are completely purified and concentrated. The fresh sulphuric acid, run through that pumice-vessel on to the nitre, acts much better than that acid which has been in the retort for hours and is charged with bisulphate, since that fresh acid contains no bisulphate in solution.

The Salpetersäure - Industrie - Gesellschaft, Gelsenkirchen (Ger. P. 180052), concentrate nitric acid up to 100 per cent. by electrolysis. The nitrogen oxides formed thereby at the cathode are introduced at the anode and there oxidised by the oxygen formed into NHO_3, after having been liquefied by cooling. Their Ger. P. 180587 describes the employment of waste acid from nitrating processes as anodic liquor in the above process. Another modification is described in their Ger. P. 184958.

Douzal (Fr. P. 396367) obtains nitric acid free from lower nitrogen oxides, and of a concentration hitherto impossible to obtain, by cooling nitrous gases, before hydration, to 24°, and then treating them with oxygen, rich in ozone, in the presence of a shower of cold water; nitrous acid is thus quantitatively transformed into nitric acid without the formation of NO.

The Elektrochemische Werke, Berlin (B. P. 15432 of 1910; Ger. P. 231546), obtain solutions of nitrogen pentoxide in monohydrated nitric acid by the electric oxidation of solutions of N_2O_4 or N_2O_3 in HNO_3. In order to prepare such a solution, containing 20 per cent. N_2O_5, a solution of 17 parts pure N_2O_4 in 80 HNO_3 is placed in the anode space, and electrolysed with platinum anodes at a current density of 200 amperes per superficial metre, and 7 vols. The oxidation is finished after 17,000 ampere hours.

Nitre-cake.

The *fixed residue* from the manufacture of nitric acid (called "*nitre-cake*," or, in the workmen's language, "sally nixon,") a corruption of "sal enixum") is practically a mixture of neutral and acid sodium sulphate. It generally contains from 25 to 30 per cent. "free acid" (*i.e.*, bisulphate acid) calculated as SO_3, and only traces of nitrate. We treat of its use in the manufacture of sodium sulphate and carbonate in detail in Vol. II., and now only remark that most of it is worked up with common salt into ordinary salt-cake and hydrochloric acid; part of it is also used up directly for glass-making, but no doubt not to great advantage. In this place we mention some other applications of nitre-cake and some processes, published since the date of the last editions of our Vol. II.

Kirkman (B. P. 5703 of 1889) employs it as an absorbent for ammonia, in which case a profitable utilisation of Na_2SO_4 will be very difficult.

Giles, Roberts, and Boake (B. P. 11979 of 1890) convert ordinary nitre-cake by addition of sulphuric acid into "pentasulphate," $Na_2O, 5SO_3, 3H_2O$, which can be packed in iron drums [?], or ordinary casks and usefully employed for certain purposes (*cf.* Uebel's "polysulphate," p. 154).

Barbier (Amer. P. 484546) dissolves nitre-cake to form a solution of 35° to 45° Baumé, and cools this down to about 10° C., by which process it is decomposed into crystallised sodium sulphate and free sulphuric acid [?].

Cheeseman (Amer. P. 714145, assigned to Agnew, Agnew and Harlow) describes a process which I long ago proposed to those interested in the matter as open to everybody, viz., neutralising a solution of nitre-cake by lime (or calcium carbonate), separating the calcium sulphate by filtration or otherwise, running off the solution of sodium sulphate and utilising this, for instance, for the manufacture of "blanc fix" (pearl hardening), by precipitation with barium hydrosulphide solution.

Bollé (B. P. 6898 of 1904) mixes the bisulphate with about 12 per cent. of wood shavings and about 2 per cent. of coke in a retort, provided with a mechanical agitator, and then heats the mixture with agitation, till all the SO_2 formed has been driven out and only neutral sulphate remains. (This is a communication from the Chemische Fabrik Grunau.)

Nibelius (Amer. P. 873070) treats nitre-cake with a volatile liquid which dissolves the acid, but not the sulphate, removes the latter, and distils the solution under diminished pressure to recover the volatile solvent, sulphuric acid remaining behind.

Parker (B. P. 24639 of 1903) brings a solution of nitre-cake into contact with a large excess of iron, thus forming ferrous sulphate and (by reduction of any nitrate present) ammonia. This solution is worked up for ferrous salt, ammonia, and sodium sulphate.

G. E. Davis (B. P. 14749 of 1903) adds to a hot concentrated solution of nitre-cake, clay, or bauxite, and heats and agitates by high-pressure steam. On cooling, a mass is obtained, suitable for sewage precipitation, etc ; but it is usually worked up by dissolving, crystallising out the excess of sodium sulphate, and then working for sodium alum.

The manufacture of sulphuric anhydride or acid from nitre-cake will be further described in Chapter XII.

Utilisation of Waste Acids from Nitrating Processes.

Enormous quantities of nitric acid, always mixed with strong sulphuric acid, are consumed in the manufacture of nitrobenzene, nitrotoluene, and other aromatic compounds required in the manufacture of colouring-matters, as well as in that of nitroglycerine, nitrocellulose, and other substances serving as explosives. The waste acids formed in the first class of processes contain but little nitric acid, generally only about 1 per cent., with about ¼ per cent. of nitrobenzene, etc. They may be used directly in the Glover tower, where the nitric acid is utilised as well as the sulphuric acid. Special processes for denitrating these acids are rarely employed, least of all with a view of recovering the nitric acid, which does not pay for the trouble and expense.

The case is entirely different with the waste acids from the manufacture of explosives. These contain much more nitric acid than those from the manufacture of nitrobenzene. Nitroglycerine waste acid contains about 10 per cent. NHO_3, 70 H_2SO_4, 20 H_2O; gun-cotton acid 11 or 12 HNO_3, 80 H_2SO_4, 8 H_2O. These acids, if it is not possible to consume them in a Glover tower, can be used for replacing part of the sulphuric acid in the nitric-acid manufacture; or else they are denitrated by steam, producing dilute sulphuric acid (which is concentrated by evaporation and used over again) and nitric acid, together with lower nitrogen oxides. By passing the vapours mixed with air through some receivers and then through a "Lunge tower," the nitrogen oxides are also converted into nitric acid, the total being recovered as nitric acid of 70° or even 80° Tw. (*cf.* pp. 164 and 168).

A detailed description of the denitrating process is found in O. Guttmann's *Manufacture of Explosives* (London, 1895) vol. ii. p. 177.

The denitration is altogether similar in this case to the process to be described in Chapter VI. in connection with the recovery of nitre in the lead-chamber process. The best kind of apparatus is a column of Volvic lava, made in one piece and packed with bits of flint, or quartz. Steam is injected to such an extent that the outflowing denitrated sulphuric acid has a specific gravity of about 1·635; it is often strongly coloured. The vapours are passed, together with air, injected or aspirated by suction, through a number of receivers, say six or eight, or else a small Guttmann battery, and then into a Lunge tower fed with a very thin stream of water, followed again by a few receivers.

Where very large quantities of nitrous vapours have to be regenerated, whether it be from waste acids of the just-mentioned kind or from other chemical processes, it is best to combine several plate-towers, one of which may be placed above the others so as to feed them with the weak acid produced therein. Thus all the recovered nitric acid can be brought up to sp. gr. 1·38. The Krauschwitzer Thonwaarenfabrik, Muskau (Silesia), furnishes this kind of plant. A very complete apparatus for this purpose has been arranged by Niedenfuhr, as described and illustrated *suprà*, p. 171.

Where sulphuric anhydride is made, these waste acids can be brought up to strength by means of SO_3 and used over again.

The following process for the recovery of nitric acid from the waste acids produced in the manufacture of nitroglycerine and nitrocellulose, as carried out at Hayle, works very well indeed. The waste acid is denitrated in a small Volvic column, standing in a strong leaden socket, with an overflow about 8 in. from the bottom. The steam-pipe must not end free in the column, but *within the liquid*, say 6 in. below its level, so that the steam rising from the liquid effects the denitration. The operation is commenced by putting water into the lead socket and passing in steam until the column is hot. Only then the feeding with waste acid is started and is conducted in such a manner that at the bottom sulphuric acid of 74 to 75 per cent. H_2SO_4 issues at a temperature of 160° C., in which case the denitration is perfect. The nitrous vapours pass first through four empty receivers, for the purpose of cooling, then successively through five Lunge towers, about 6 ft. high, and then through eight receivers, charged with 6 in. of water each. The towers are fed very slowly with water, the holes in the covers being plugged up with wood in such a manner that the water trickles down in drops. On the top of the first tower one of the holes is left open in order to draw in the necessary air. Thus the towers yield nitric acid of 57 to 64 per cent. HNO_3, inclusive of 1·5 per cent. N_2O_4, on the average of sp gr. 1·40. The water in the receivers is left there until the specific gravity reaches 1·37. This plant denitrates 10 tons of waste acid per diem.

Pauling (Amer. P. 898390) concentrates waste nitrosulphuric acid by placing it in the anode compartment of an electrolysing apparatus, the cathode compartment being filled with dilute nitric acid. The nitrogen oxides liberated at the cathode are conducted into the anode chamber.

(*Cf.* also *suprà*, p. 168, the process of Hirsch and several others.

Various other Processes for the Manufacture of Nitric Acid.

Glock (Ger. P. 110254) heats nitrate in a pan provided with stirring-gear to 120° to 150° and runs in the equivalent quantity of sulphuric acid, previously heated to 100° to 130°, in a thin jet. The end of the decomposition is facilitated by steam or a thin jet of water. At last air is blown through, whereupon the solid, pulverulent neutral sodium sulphate is ladled out. Or else the nitrate is from the first heated to 250° C. [This process looks extremely impracticable.]

Manufacture of Nitric Acid without Sulphuric Acid.—Campbell and Walker (B. P. 9782 of 1894) grind nitre-cake with nitrate of soda and charge the mixture into retorts provided with a mechanical agitator.

Garroway (B. P. 6777 of 1899; *J. Soc. Chem. Ind.*, 1901, p. 1191) mixes ordinary acid nitre-cake with sodium nitrate, heats the mixture in a retort, and blows a spray of weak nitric acid by means of compressed air over the mixture. The nitrogen oxides, mixed with steam and air, are regenerated by condensing-tubes and towers into nitric acid. It is alleged that ultimately a 96-per-cent. acid can be produced. The residue is neutral salt-cake, testing 98·36 per cent. This process is stated to have been worked for three years at Glasgow.

Garroway (B. P. 2466 of 1895) also prepares nitric acid by heating a mixture of nitrate of soda and ferrous sulphate or alum, obtaining sulphate of soda and oxide of iron or alumina. He also patents the decomposition of sodium nitrate by silica (B. P. 2489 of 1896).

Very interesting are the processes intended for decomposing nitrate of soda in such manner that, besides nitric acid, caustic soda is formed. Theoretically these processes are enormously superior to the ordinary process; there is no waste of sulphuric acid and no production of nitre-cake, which is a product of very low value, but the soda is converted into its most valuable form, as caustic or carbonate. But not one of these processes has come into regular use. They all suffer from the drawback that the temperature of decomposition is too high, which necessitates special shapes of retorts and great wear and tear of these, and that some of the nitric acid (often a very considerable proportion) is reduced to lower oxides. These can be reconverted into nitric acid by means of intimate contact with air or water, in "plate-columns" (Lunge towers) or otherwise; but this cannot be done without a perceptible loss, and it never leads to the production of very strong nitric acid, such as is required for the manufacture of explosives and many other purposes.

We therefore only refer to the enumeration of these processes in Vol. III. (second edition), pp. 254 *et seq.*, and briefly quote the more recent additions to the subject.

A special retort for the Lunge and Lyte process (decomposition of $NaNO_3$ by Fe_2O_3) has been constructed and patented (Ger. P. 90654). It consists of a revolving cylinder placed in a sloping position, with inner projections and contrivances for feeding and exhausting without stopping the process. A full description of the whole process has been given by J. L. F. Vogel in the *Eng. and Min. J.*, 1900, p. 408.

Main, Stevenston, and M'Donald (B. P. 23819 of 1895) heat sodium nitrate with manganese oxides. Garroway (Ger. P. 79699) employs lime and superheated steam. Vogt (B. P. 22018 of 1891) heats with lime, ferric, or manganese oxides in a current of superheated steam and carbon dioxide.

Hemingway (Amer. P. 781826) manufactures nitric acid by mixing nitrate of soda, sulphuric acid, and water, heating the mixture to 77° and gradually adding ferrous sulphate. Ferric sulphate and sulphate of soda are obtained as by-products. The nitrous vapours are condensed in the usual manner with the admixture of air.

Blackmore (for Robinson and Spruance, Amer. P. 982466) exposes barium nitrate to the action of superheated steam, whereby BaO_2 and nitric acid are formed.

Guye (Fr. P. 389864) obtains nitrophosphates, for application as manure, by passing mixtures of air, with very small quantities of nitrogen oxides, over tricalcic phosphate, in the presence of sufficient moisture. Thereby mixtures of di- and monocalcic phosphates with calcium nitrite and nitrate are formed.

The Chemische Werke vorm. Byk (Ger. P. 208143) make concentrated nitric acid from calcium nitrate by adding concentrated sulphuric acid, and separating the liquid from the $CaSO_4$ formed by filtering, pressing, or centrifuging. The same process is described in the Amer. P. 928545. According to Ger. P. 217476 they bring about the decomposition of the calcium nitrate by the theoretical quantity of sulphuric acid in the presence of so much water that nitric acid of not essentially more than 59 per cent. HNO_3 is formed. The advantage of this modification is that the time of filtration is very much reduced, as hydrated calcium sulphate allows the liquid to pass through rapidly, and the channels are not stopped up by the hydration. Moreover more concentrated nitric acid is thus obtained, because the gypsum combines with 2 mols. of water. They dissolve 100 parts of Notodden nitre in nitric acid of 55° B. and add sulphuric acid until no more calcium sulphate is precipitated (Fr. P. 400305).

Dieffenbach and Moldenhauer (Amer. P. 914813; Fr. P. 389500) convert hydrocyanic acid into oxides of nitrogen, by passing it, mixed with oxygen or air, overheated catalysers, such as Pt, Pd, Ir as MnO_2, by which the combustion is effected at a temperature below that at which the nitrogen oxides are destroyed.

Nitric Acid from Atmospheric Nitrogen.

In the nature of things, the Chilian and other beds of native nitrates are doomed to exhaustion, sooner or later, and long before this takes place, the price of nitric acid, if depending upon that raw material alone, would have risen to a dangerous height. Hence it is a matter of course that numerous efforts have been made for some time past towards utilising the inexhaustible store of nitrogen, present everywhere in the shape of atmospheric air, for the manufacture of nitric acid, which is all the more a most natural aim, as the other ingredients for the process, viz., free oxygen and water, are likewise present everywhere, and are to be had for nothing.

The problem is merely to find out profitable ways for bringing about the reaction: $N_2 + 5O + H_2O = 2HNO_3$, which evidently does not easily take place by ordinary means—fortunately for all organised beings, since otherwise the atmospheric air would have become unbreathable long ago. We shall now see what ways have been tried for that purpose.

A. *Oxidation of Nitrogen by the Action of High Temperatures.*

Already in the ordinary processes of combustion, *e.g.* by the action of high temperatures, a very slight quantity of nitrogen is oxidised, but far below that which would enable a technical process to be founded thereon. The following patents try to do so anyhow, all the more since Bunsen, in 1849, noticed that nitric acid is also formed in the explosion of fulminating gas.

We shall now enumerate, first, the processes intended to produce nitrogen oxides from atmospheric air, or other mixtures of free nitrogen and oxygen, by the application of heat in the ordinary manner, sometimes with aid of catalytic substances, and then pass on to those which make use of electricity for that purpose.

Pawlikowski (Ger. P. 171623) compresses the gases in a cylinder and causes them to unite by explosion inside or outside the cylinder. A secondary electric energy may be introduced as well from without (B. P. 25728 of 1905).

Brünler and Kettler (Ger. P. 185094; B. Ps. of Brünler 5852 and 5901 of 1906), Fig. 40, describe a furnace *d* of globular shape, made of magnesia, with a bottom pipe *h* dipping in water contained in an outer cylinder *a*, capable of resisting high pressure. The gases containing oxygen are passed into the inner globe by means of lateral pipes, etc., together with fuel gases *f,f*; the apertures of these pipes are opposite each other, so that strong whirls are produced, a perfect combustion of the fuel gas is obtained, and temperatures of 3000° are reached near the walls of the globe *d*, and even higher ones more inside. Nitrogen is blown in from the top at *g* at such a rate that the temperature cannot sink below that which is best for the oxidation of N. The gases and steam formed by combustion escape through a valve (*c*) at the top, and the water containing nitric acid is let out at the bottom of the cylinder.

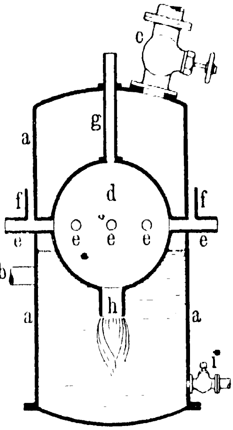


FIG. 40.

The same inventors (Ger. Ps. 205351 and 205538; Fr. P. 380467) blow, together with O and N, also some fuel, gaseous or liquid, or in the state of powder, into the furnace, which at one end dips in water, so that the products of combustion are immediately taken up by this. For instance, petroleum is burnt in a chamber, open at the bottom and there dipping into water, air being passed into the chamber under pressure. The dimensions of the chamber and the velocity of the gas current are regulated in such manner that the pointed flame of the burning gases penetrates into the water. The best results are obtained by burning under increased pressure.

The Chemische Fabrik Griesheim-Elektron (B. P. 13954 of 1907) produces catalytic bodies, especially intended for use in the manufacture of nitric acid, by heating a carrier, coated with platinum-black (and, if necessary, before this coated with a glaze) to a temperature at which the platinum sinters.

Bender (B. P. 8653 of 1907; Fr. Ps. 377442 and 405463; Amer. P. 900471; Ger. P. 192883) heats the air by means of an oxyhydrogen flame and increases the formation of nitrogen oxides by cooling the products of combustion by means of blowing in superheated steam, and then less heated steam. The partial dissociation of the steam furnishes a mixture of O and H, which is utilised for the heating process. The production of NO, according to him, amounts to 2·9 per cent. His Ger. P. 217550 prescribes burning the atmospheric nitrogen in an upright furnace, fired with hydrocarbons, which enter through holes in a circular tube near the bottom, and are conducted upwards by these tubes, at the upper end of which they take fire. The air entering from below cools these tubes and is preheated by them. The same inventor's Ger. P. appl. B. 51927 prescribes the application of fuel which furnishes notable quantities of water on burning. His B. P. is 18203 of 1909 Other patents of his are Ger. Ps. 217079, 217080, and 227490.

Kettler (Ger. P. 209961 ; Fr. P. 396161 ; B. P. 24264 of 1908) places in the furnace a platinum or porcelain coil, through which passes the mixture of O and N from the bottom upwards, being heated to 1200° to 1300° by a burning mixture of air and illuminating-gas or benzene or petroleum vapours. In a horizontal tube, branching off at the top of this furnace, the air is heated further, up to 2000°, by the combustion of benzene vapour with oxygen, and still more by blowing in acetylene gas and oxygen. The gases now pass through an inclined, perforated tube, into which the absorbing-liquid enters from without.

Dupré (Ger. P. appl. D19353) passes air over a mixture of manganous and sodium carbonate at temperatures below the fusing point of the mixture; the nitre formed is obtained by lixiviating the mixture, and the higher manganese oxides formed are utilised for the manufacture of chlorine.

Vietinghoff-Scheel (Ger. P. 222629) burns C—or H—containing substances in mixtures of O and N in the presence of catalytically acting substances, such as NaF, or CaF_2, or Fe, Cu, and Ni, as metals or oxides, or MgO, CaO, Al_2O_3, or SiO_2, blown into the gas-space in the form of powders, in order to produce nitrogen oxides. The above-mentioned catalysers appear to be efficient for that purpose in proportion to their capacity for the emission of light.

Södermann (Fr. P. 413117) burns a mixture of N and O in a tube, in the walls of which, at any desired point, a cooling liquid or gas is circulated; a mixture of "N_2O, nitrogen protoxide, and NO, nitrogen binoxide as a secondary product" is thus produced, the proportions depending upon the particular zone of the flame. In an addition to this patent, claim is made for the introduction of acetylene or other gaseous hydrocarbon into a flame of N and O, with subsequent rapid cooling of the reaction products.

Södermann (Fr. P. 416036) heats a mixture of O and N, first in a spiral platinum tube to about 1400°, then in a horizontal extension, heated by burning hydrocarbon vapours with air enriched with oxygen, to 2000°, then passes the gases into an inclined sheet-iron reaction-pipe, immersed in limewater, and here brings up the temperature to 2700° to 2600°, either by introducing a little acetylene or by means of an electric arc. Through holes in the upper part of the pipe, a shower of absorbent liquid may be admitted at will, in order to suddenly cool the gases after the reaction.

Hausser (B. Ps. 12401 and 13989 of 1906; Ger. P. 216518; Amer. P. 961350; Fr. P. 409758) produces oxides of nitrogen by the explosive combustion of a compressed mixture of N, O, and a suitable combustible gas or vapour, followed by chilling the mixture by injection of water, etc., or by passing it into a cooled receptacle. According to his B. P. 27826 of 1906 the bombs are rinsed after the explosion with air from a compressor, and the compressed mixed gases are caused to enter a receiver, from which a number of explosion bombs can be filled. His Ger. P. 232569; Fr. P. 420112; Amer. P. 1000732 prescribes keeping the explosion pressure constant, or nearly so, until the thermic equilibrium has been attained. This can be achieved either by employing a sufficiently large bomb, or by protecting this against radiation of heat. By exploding a mixture of 89 to 90 per cent. air with 10 to 11 per cent. illuminating gas in bomb of 100 l. capacity gases containing 1·3 to 1·7 per cent. NO were obtained. His B. P. 13989 of 1907 compresses the combustible gas with an excess of air and effects the explosion in another vessel. His B. P. 20777 of 1910 shows how a temperature of 1600° to 1700° C. (absolute) can be reached by exploding a mixture of about 10 vols. illuminating-gas with 90 vols of air.

Otto Pfennig's Erben (Ger. P. 229142) blow gaseous fuel, mixed with superheated oxygen or air, under pressure through a slit-burner into the furnace, which is adapted to the shape of the flame disc. The two furnace walls parallel to the flame disc are perforated by many holes in the place where the greatest heat is developed.

R. P. Pictet (Ger. P. 226687; Fr. P. 415594), starting from the observation that in certain spots of the flame the action of O upon N produces considerable quantities of nitrogen protoxide, prevents this by producing a strong and sudden fall of temperature in that place where the maximum of N_2O would be formed. According to his Ger. P. 226867 that N_2O can be utilised for the manufacture of explosives.

The Badische Anilin- und Sodafabrik (Fr. P. 396375; B. P. 20406 of 1908; Ger. P. 219494) produces oxides of nitrogen by burning carbon monoxide in an atmosphere containing N and O under pressure. For the rapid cooling of the products, in order to prevent the decomposition of nitrogen oxides, a long pointed form is given to the flame, and it is made to lick the sides of the tube, its point being directed against a cold surface. Before allowing them to expand, the gases are further cooled, so as to furnish liquid or solid nitrogen peroxide; or concentrated nitric acid is prepared directly by the addition of sufficient steam, or hydrogen, or other combustible to the gases before combustion. The refrigeration may be effected by the expansion of gas already refrigerated, and the heat produced by combustion may be utilised in obtaining the required compression.

Phillips and Bulteel (B. P. 23976 of 1909) blow air and powdered fuel tangentially into an annular combustion furnace; the gyratory motion imparted to the burning fuel raises the temperature to such a degree as to induce the formation of nitrogen oxides from the atmospheric N and O, or of NH_3 in the presence of aqueous vapour. Their B. Ps. 27558 of 1910, 29893 of 1910, and 4268 of 1911 describe other methods of spreading out the flame over a large surface.

Devilaine (Fr. P. 423893) obtains nitric acid, sulphuric acid, and many other substances, by the employment of ultra-violet rays of various origin as oxidising agent.

The Société l'Air liquide (Fr. P. 416557) heats a mixture of N and O strongly under pressure and then allows it suddenly to expand, in order to cool it rapidly. It employs for this purpose a metallic cylinder, in the centre of which is a thin-walled magnesia tube, the space between the tubes being filled with powdered magnesia or the like. The heating may be effected electrically or by combustion.

Wiegolanski (Norw. P. 20328) heats air to 1500° to 1700° and cools it suddenly down to 1200° by means of NO_2, heated to 500°. The NO_2 easily gives off oxygen which *in statu nascendi* oxidises the N without the aid of electricity.

Special means for avoiding the retrogression of chemical reactions by high temperatures are described by Scherbius in Ger. Ps. 213709 and 221129.

Price (B. P. 10755 of 1909) manufactures nitrates and nitrites by conducting N and H, in the proportions in which they form NH_3, into saturated solutions of basic substances at low temperature and pressure, whereby the salts obtain the necessary O from the aqueous solution, which releases H to be used from time to time with fresh supplies of N. His B. P. 5657 of 1910 describes the preparation of ammonium nitrate by subjecting air, mixed with H_2O in the gaseous states or the gases constituting H_2O, and additional supplies of O, to great heat, then suddenly cooling and liquefying them.

The Salpetersaure-Industrie-Gesellschaft, Gelsenkirchen (Ger. P. 235299), subject highly heated air or other mixtures of O and N to expansion, keeping up the same temperature, in such manner that the velocity of reaction is diminished without cooling the gases. For this purpose they attach to the air-heating furnace a vessel, evacuated below a pressure of 400 mm. mercury, with an arrangement for protecting the gases against cooling during their passage into that vessel and during the expansion. This process avoids the decomposition of NO, otherwise taking place in consequence of the extremely high velocity of reaction and the extremely high temperatures thereby produced.

The same firm (Fr. P. 420252) employs a furnace, made of magnesia, divided into two compartments, communicating at the top. Air is heated to 2000° in one compartment, and the pressure in the other is reduced by an air-pump to 400 mm. of mercury. In the upper part there is a heat-compensating apparatus, such as an electric arc playing between water-cooled platinum electrodes, so that the sudden expansion of the highly heated nitrogen oxides takes place adiabatically, and the lower part of the compartment is provided with a refrigerating appliance, so as to prevent dissociation of the nitrogen oxides formed.

The Westdeutsche Thomasphospatwerke (Ger. P. 182297) heat a mixture of air and steam to such a degree that the steam is dissociated to a great extent. The hydrogen thus formed is removed before the gaseous mixture cools down, by diffusion through porous walls, so as to avoid its reducing-action on the NO formed.

Pauling (Amer. P. 758774) heats the air by an oxyhydrogen flame and removes the free hydrogen, present in excess, by means of chlorine. His Fr. Ps. are 323760 and 325244.

B. *Oxidation of Atmospheric Nitrogen by Means of Electricity.*

As early as 1775[1] Priestley made an observation on the action of electricity on atmospheric air, which later on he justly interpreted as having produced nitrous acid. About 1781 Cavendish found that hydrogen, on burning in an excess of air, yields water containing nitric acid. In 1786 he showed that all the nitrogen of a certain quantity of air can be burned by adding an excess of oxygen, and allowing electric sparks to play upon the mixture. In publishing his observations in 1785, he expressly acknowledged the priority of Priestley in that respect. But a century elapsed before the attention, first of scientists and then that of technologists, was again directed to that subject; stimulated to a great extent by the recognition of the fact that the rapid increase of mankind requires a corresponding increase in the production of foodstuff of all kinds, in the first line of corn; that such an increase to the required extent is only possible by the application of artificial nitrogenous fertilisers, principally of nitrates, and that the natural sources of nitrates in Chili and elsewhere, if called upon to the corresponding extent, would be exhausted within a generation or two.

It has been known for a long time that after thunderstorms a notable quantity of ammonium nitrate and nitrite is found in the air, and that this is of great importance for the fertility of the soil receiving the rain water, but during a long time apparently no efforts have been made to utilise artificially produced electrical discharges in that direction.

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[1] Apart from my own notes, I follow in this historical survey mainly the paper of K. Birkeland on the above subject, published in *The Transactions of the Faraday Society*, vol. ii., September 1906, from which I take also the account of the Birkeland and Eyde process. Also the paper by O. N. Witt in *Chem. Ind.*, 1905, pp. 761 *et seq.*

In 1880 Spottiswoode and Dewar studied the action of electric flames in air. In 1892 Crookes followed in that way, and showed the production of nitrous and nitric acid thereby. In 1897 Lord Rayleigh (*J. Chem. Soc.*, lxxi. pp. 81 *et seq.*) published his observations on the oxidation of nitrogen, which led him, in collaboration with Ramsay, to the discovery of argon. From his laboratory experiments he concluded that one kilowatt hour would be required to form 50 g. of nitric acid. He also mentions the electrical difficulty met with in producing a steady high-tension flame for oxidising nitrogen, a question second in importance only to that of obtaining the highest possible output. Lord Rayleigh was the first to show that with electric arcs it is possible to fix nitrogen almost in proportion to the electric energy expended.

Crookes (*Electr. World*, xxxiii. p. 319) in the same year, by means of induction sparks, succeeded in forming 74 g. $NaNO_3$ by the expenditure of one kilowatt hour, *i.e.*, 1 ton of $NaNO_3$ by 14,000 kilowatt hours. That means the generation of so much power that it is out of the question to use steam for that purpose, and even water-power would be too expensive except under specially favourable conditions.

Important contributions to the object in view by laboratory investigation, and by theoretical reasonings, were now made from many sides. We here mention:

Muthmann and Hofer (*Berl. Ber.*, 1903, p. 438); Lepel (*Berl. Ber.*, 1897, p. 1027; 1903, p 1251; 1904, p. 3470); Stavenhagen (*Berl. Ber.*, 1905, p. 2171); Grau and Russ (*Wiener Akad. Ber.*, December 1906; *Z. Elektrochem.*, 1907, p. 573); Nernst (*Z. anorg. Chem.*, 1906, pp. 213 and 229); Berthelot (*Comptes rend.*, cxlii. p. 1867); Brode (*Z. Elektrochem.*, 1905, p. 752); Scheuer (*ibid.*, 1905, p. 565); Bodenstein (*Z. angew. Chem.*, 1906, pp. 14-21); Haber, with various collaborators, Coates, Makowetzky, Holwech, Koenig, and Platou (*ibid.*, 1907, p. 725; 1909, p. 689; 1910, pp. 684, 789, 796, 803, 810; *Z. physik. Chem.*, 1909, p. 337); Warburg and Leithäuser (*Berl. Akad. Ber.*, 1907, p 229; *Ann. Physik* [4], xx. p. 743; *Chem. Centr.*, 1907, ii. 43); Fischer and

Braehmer (*Berl. Ber.*, 1906, pp. 940-968); Fischer and Marx (*Berl. Ber.*, 1906, p. 2557); Häusser (*Z. Elektrochem.*, 1906, p. 444); Briner and Durand (*Comptes rend.*, cxlv., p. 248); Birkeland ("Faraday Lecture," July 1906, *Trans. Far. Soc.*, 1906, vol. ii.); Holwech (*Z. angew. Chem.*, 1908, p. 2131; *Z. Elektrochem.*, 1910, pp. 369-390); Grau and Russ (*Z. angew. Chem.*, 1908, p. 554); Russ (*ibid.*, 1908, p. 555); Howles (*J. Soc. Chem. Ind.*, 1907, p. 290); Le Blanc (*Z. Elektrochem.*, 1907, p. 297); Guye (*Monit. Scient.*, 1907, p. 225); Bodenstein (*Z. Elektrochem.*, 1910, p. 876); Forster and Blich (*Z. angew. Chem.*, 1910, p. 2017).

Already in 1903, Muthmann and Hofer maintained the view that the oxidation of nitrogen in electric arcs is exclusively an effect of heat, and that there exists in the arc a chemical equilibrium between oxygen, nitrogen, and nitric oxide. Nernst, Brode, Haber, and others have worked in the same direction. Birkeland puts the matter in this way: a mixture of 1 kg. oxygen with 3·3 kg. nitrogen at ordinary temperatures forms a certain quantity of NO, but only to an infinitesimally small extent, and even at 700° is almost nothing. This increases with the temperature, and at 3000° should be 5 per cent. of the air. If cooled down slowly, gradually the NO will diminish to the amount corresponding to each temperature, and at 700° it will be again nearly = nought. If, however, the cooling takes place very rapidly, the NO remains, and this is a point to be observed in all attempts made at producing the combination of N and O by effects of heat, whether electrically or otherwise.

Laveth and Rand (*Z. angew. Chem.*, 1905, p. 1906) give the following table of the yields of nitric acid from air by various electrical methods, the figures denoting grammes of HNO_3 per kilowatt hour:—

Year.			Year.		
1897.	Rayleigh . . .	41·1	1897.	Crookes . . .	74·0
1900.	MacDougall and Howles	33·8	1902.	Bradley and Lovejoy	83·0
1902.	Kowalski . . .	55·0	1904.	Birkeland and Eyde .	110·0
1903.	Muthmann and Hofer	70·0			

The theoretical maximum, according to Muthmann and Hofer's calculations, is 157·5 g. HNO_3 per kilowatt hour. The authors consider that indirect methods for the fixation of nitrogen by means of an intermediate product, as nitride or cyanamide, are more likely to lead to an economical, commercial success.

A very interesting paper on the fixation of atmospheric nitrogen is that of Ph. A. Guye in *J. Soc. Chem. Ind.*, 1906, pp. 567-574 We abstract here only that part of it which refers to nitric acid and nitrates, leaving aside the fixation of N as cyanamide and NH_3. The importance of the problem is shown by the fact that in 1905 the consumption of Chili nitrate has been 1,567,000 tons, of which about 300,000 tons has been utilised in chemical industry, the balance as manure. Crookes estimates that the quantity of nitrate necessary to meet the yearly increasing demands will be more than 12,000,000 tons after thirty years or so; long before this the Chili beds would be exhausted (*cf.* p. 125). The value of 1 kg. N as Chili nitrate is at present 1s. 3d., as sulphate of ammonia 1s. 2½d., as nitric acid 1s. 7½d. Concerning the fixation of atmospheric N in the shape of nitric acid by electrochemical processes, many contradictory statements have been made as to the scientific and commercial aspect of this problem, but it is now certain that the phenomenon is strictly governed by the law of chemical dynamics. So much is certain that it is necessary to work at a high temperature in order to increase the efficiency and velocity of the reaction, and that the resulting gases must be cooled instantaneously to avoid the reverse of the reaction. They contain 1 to 2 per cent. of NO by volume, as they pass out of the arc chamber, and must then be treated in order to transform the NO into nitric acid, or nitrates, or nitrites. The cost of this process is very different, according to circumstances. At present we may take a production of 500 kg. HNO_3 per kilowatt year as a fair average. From the results, obtained at a plant in Norway, the author calculates the cost price of a ton of HNO_3, in the shape of concentrated acid, £12, 2s., or 11½d. per kg. N, which shows a good margin when compared with the above-mentioned price of nitric acid. The discussion at the close of reading this paper, in which several of the greatest authorities took part, was also most interesting, but we must, apart from the consideration of space, all the more abstain from quoting more details, as the author himself admitted the "purely comparative," *i.e.*, hypothetical, nature of the figures given.

In *Bull. Soc. Chim.*, Oct.-Nov. 1909, Guye claims for Briner and Durand priority with respect of obtaining high concentrations of nitrogen oxides by such processes; this claim is strongly contested by Haber, Koenig, and Platou in *Z. Elektrochem.*, 1910, p. 790.

Neuberger (*Z. angew. Chem.*, 1905, pp. 1873 *et seq.*) gives an historic survey of the production of nitrogen oxides from air by electric discharges.

Cramp and Hoyle (*J. Soc. Chem. Ind.*, 1909, p. 95) discuss that question on the strength of laboratory experiments. They found that changes of yield to the extent of 50 per cent. occurred by slight variations of the spark gas, the strength of current, and the air-flask. For a given current the maximum yield of acid does not correspond with the maximum concentration of acid, and the value of a magnetic fixed for spreading out the flame, as in the Birkeland-Eyde processes, is doubtful.

Ehrlich and Russ (*Sitzungsberichte der kais. Akad. d. Wiss. in Wien*, vol. cxx., July 1911; *Monatsh.*, 1911, pp. 917-996) made a detailed investigation on the process of the oxidation of nitrogen by silent electric discharges in the presence of ozone. Under the conditions chosen by them they obtained the following values:—

Percentage in oxygen by volume of the initial mixture.	Maximum of NO obtained in vol. per cent. in the final gas.
5	[0·2]
20·8	4·1
50	13·2
75·0	18·0
91·5	[21]

Such high results are not produced by the electric equilibrium of nitric oxide, but by a combination of electric and chemical action, since ozone present in excess oxidises the NO formed to N_2O_5 and thus brings about a further formation of NO. The latter proceeds up to the point when all ozone has been used up; further discharges decompose the N_2O_5 with formation of NO_2, and the latter is then almost completely dissociated until a stationary point is reached, which depends on the one hand to an electric equilibrium of NO corresponding to the conditions of the experiment, on the other hand on the velocity of the formation of ozone. The phenomenon known as "poisoning," by which even small quantities of NO_2 prevent the formation of NO, is connected with this. With an increase of the initial concentration of oxygen the available quantity of ozone is also increased, and together with this the attainable maximum formation of NO up to the oxidation of all the nitrogen. Above this point a stationary point is reached for the N_2O_5 and ozone, but generally the maximum of the latter has been reached much earlier. At given electric conditions the velocity of the formation of NO is within very wide limits independent of the composition of the original mixture and nearly constant, but the velocity of the formation of ozone increases with the increase of oxygen in the original mixture. In gases containing but little nitrogen the velocities are smaller, probably owing to diminished conductivity. A variation of the electric conditions, when employing the mine composition of gases, alters the velocity of the formation of NO and of ozone in the same sense. An increase of energy or a decrease of the gaseous pressure produces lower values for NO. The dissociation of ozone hastened by N_2O_5 is within certain limits independent of the concentration of ozone.

The work done on this subject in the Karlsruhe laboratory by Haber and his co-operators (*vide* the literature on p. 209) is of the greatest importance. A summary is given here, from notes supplied by Professor Haber to the author. The fact that by working under diminished pressure higher concentrations of NO can be obtained than at ordinary pressures was securely established. But that style of working entails several difficulties, if intended to be carried out on a large scale. Haber obtained with the cooled alternate current per kilowatt hour: 3·4 per cent. NO and 57 g. HNO_3; at 2 per cent. NO, 75 g.; at 2·5 per cent. NO, 80 g. HNO_3. By this means higher concentrations are obtained for the same yield, and higher yields for the same concentration. But the difficulty of providing such cooled arcs on the large scale is much greater than that of producing uncooled arcs. Since in many cases carbon monoxide is obtained as a by-product, *e.g.* in the manufacture of calcium carbide, the possibility of carrying out the process must be judged according to local circumstances. Up to now, no experience on the large scale has been made with Haber's process.

Morden (*infrà*, p. 224), on repeating Haber's experiments in his laboratory, obtained the best yield at a pressure of 400 mm., and at a low voltage, viz. 92 g. HNO_3 per kilowatt hour.

Technical Processes for the Manufacture of Nitrogen Oxides and Nitric Acid or Nitrates by Means of Electrical Currents.

Concerning the technical side of the question, we shall in the first instance quote a number of patents and other publications, about which we must refer the reader to the originals, and we shall then give short abstracts of those patents, etc., which seem to deserve a special notice, reserving a more detailed treatment to the small number of inventions which have been carried out on a really large scale and survived the first efforts of calling them into life.

Prim (Ger. P. 20722); Schneller and Koelemann (Ger. P. 173519); F. De Mare (Ger. Ps. 174177 and 176036); Initiativkomitee für die Herstellung von stickstoffhaltigen Produkten (*Fischer's Jahresber.*, 1906, p. 457); Hausser (B. Ps. 12401 of 1906 and 13989 of 1907; *Z. Ingen.*, 1906, p. 298); Marquardt and Viertel (Amer. P. 804021); Pauling and the Gladbeck Chemical Co. (Ger. P. 152805; Amer. Ps. 758774 and 758775; Fr. P. 341109; Swiss P. 31189); Petersson (Ger. Ps. 183041 and 185897); A. de Montlaur (Ger. P. 188750); Société anonyme d'études électrochimiques (Ger. Ps. 187585 and 180290; Austr. P. 23371); Société anonyme d'électricité et d'automobiles (Ger. P. 180290; *Chem. Ind.*, 1908, p. 87); Tanne and Papenbruch (Fr. P. 367440); Thoresen and Tharaldsen (Fr. P. 352556); Chem. Fabrik Buckau (Fr. P. 370977); Fr. Fischer (*Chem. Zeit.*, 1906, p. 1292; *Z. Elektrochem.*, 1906, p. 525); Fr. Foerster (*Z. Elektrochem.*, 1906, p. 529); Klaudy (*ibid.*, p. 545, with a rectification on p. 712); Neuburger (*Z. angew. Chem.*, 1906, p. 977); Wood (Amer. P. 826301; *Chem. Ind.*, 1908, p. 91); Mitchell and Parks (Amer. Ps. 773407 and 817082; *ibid.*, p. 91); Mehner (B. P. 28667 of 1903); N. Caro, *Die Stickstoffrage in Deutschland*, 2nd edition (pamphlet), 1908; Polzenius (Austr. P. appl. 5210); Farbwerke vorm. Meister Lucius and Brüning (B. P. 10522 of 1911); Steinmetz (Amer. P. 894547); *Z. Elektrochem.*, 1907, pp. 75-77, 190-198, 210-221, 225-234, 237-255, 280-286 (with many illustrations); Hölbling and Preiss, in *Chem. Ind.*, 1908, pp. 83 *et seq.*; P. F. Frankland, *J Soc. Chem. Ind.*, 1907, pp. 175 *et seq.*

In 1895, Naville and Guye, in Geneva, took out a patent (Ger. P. 88320) for making nitric acid by electrolytic methods, but without practical success. Their later efforts in that direction will be mentioned *infrà.*

Darling and Forrest (B. P. 5808 of 1894) produce nitric acid by electrolysing fused alkaline nitrates, metallic K or Na being obtained at the same time. Their B. P. 13171 of 1895 extends this process to the production of nitrogen oxides for the manufacture of sulphuric acid, together with caustic soda.

Siemens Brothers (Ger. P. appl. S16610 of 21st June 1902) protect the production of nitrogen oxides from mixtures of N and O by means of cooled metallic electrodes.

Rasch (*Z. Elektrochem.*, 1903, p. 162) proposes for pyrochemical reactions generally, and specially for the preparation of nitric acid from atmospheric air, the employment of conductors of the second class (metallic oxides and other metallic compounds) which are very stable and stand very high temperatures. Special apparatus for the oxidation of free nitrogen to nitric acid is described by Pauling (Ger. P. 152805); Lepel (*Berl. Ber.*, 1904, pp. 713 and 3470); Wiesler (*Z. angew. Chem.*, 1904, p. 1714).

M'Dougall and Howles (B. P. 4643 of 1899) applied Lord Rayleigh's method (*suprà*, p. 209) for work on a larger scale. They got up to a yield of 49·2 g. HNO_3 per E.H.P. hour. They found that it is better to work at ordinary temperatures than in the heat; that the intensity of current in the electric arc should not exceed 0·15 to 0·2 ampère; they employed electrodes of platinum-iridium, which were but little acted upon.

Kowalski and Moscicki (B. P. 20497 of 1903; Amer. P. 754147), having observed that the output of NO with a large number of periods is better than with the usual number of periods from an ordinary alternator, oxidised nitrogen in high-tension flames of up to 50,000 volts with oscillating currents of from 6000 to 10,000 periods per second. But Birkeland (*loc. cit.*) found that he could not detect any difference of the output in flames produced according to their system and those employed in the Birkeland-Eyde process. The factory built on Kowalski and Moscicki's plan had been stopped already in 1905 (Witt, *Chem. Ind.*, 1905, p. 703).

Bradley and Lovejoy (B. P. 8230 of 1901; Amer. Ps. 709867 and 709868) produce nitric acid from atmospheric air by means of an electric arc, subdivided in such manner as to obtain a large surface by the expenditure of a small amount of electric energy. Their process was taken over by the Atmospheric Products Co., working with a capital of £200,000, and disposing of water power at Niagara Falls to the extent of 2000 h.p. Their apparatus is described in *Electrochemical Energy*, vol. i. p. 20. They employ a continuous current, which first plays in sparks between two platinum electrodes, forming a light-arc which is at once interrupted; when again closing the circuit, the play goes on again, and so forth. There are twenty-three rows of six fixed electrodes each, and the same number of electrodes revolving round a perpendicular axis, moved by an electromotor with 500 revolutions per minute. Thus there are formed 6 × 500 = 3000, altogether 3000 × 138 = 413,000 light-arcs per minute, produced by a revolving interruptor. The apparatus is surrounded by a casing into which 2·3 l. air per minute can be introduced for each electrode Three hundred and eighteen litres air per minute enter the casing, are partly acted upon by the light-arc, and are drawn out by an exhauster. The air now contains 2·5 volume per cent. of NO_2, which is converted in a tower by the action of water into $HNO_3 + HNO_2$. The yield for 7 h.p. hour is 1 lb. = 0·45 kg. nitric acid.

Another patent of Bradley and the Atmospheric Products Co. (Amer. P. 829874; Ger. P. 179288) proceeds in a different way. They now aim at drawing out an electric arc as long as possible, and produce this by an alternating current, without losing the advantages of the continuous current, by employing a very high electric tension and self-induction. The gases are furnished with an excess of oxygen and hydrogen, whereby the yield of nitric acid is to be increased. In *Chem. Ind.*, 1908, p. 86, it is stated that these processes have turned out uneconomical, probably owing to insufficient regard being paid to the influence of pressure and temperature, and to the fact that each furnace works up only 300 l. of air per minute (against 25,000 l. in the Birkeland furnaces), which means a very great number of furnaces, and corresponding expenses. Schönherr (*vide infra*) states that only one apparatus was built on that system and stopped in 1904. The United States Census Bulletin, No. 13 (quoted in *Chem. Ind.*, 1909, p. 44) also states that these processes were given up in the summer of 1904 as they did not pay. Birkeland, in his afore-mentioned paper, considers their failure as due to the distribution of the electric energy over too many *small* arcs, although it seems wise to effect that distribution over a large number of variable arcs of short duration, which allows to keep the energy consumed in the arcs to be kept fairly constant without the necessity of employing great inductive resistance.

Helbig (B. P. 3346 of 1905; Ger. P. 189864), in the manufacture of nitrogen oxides from atmospheric air by means of the electric light-arc, utilises the well-known fact that the oxides of calcium or magnesium very considerably increase the electric conductivity of gases. If the electrodes are surrounded by a jacket of MgO or CaO, the arc may be formed with the very low tension of 300 to 600 volts; the arc spreads out and fills the whole of the space, so that the gases are very evenly heated. Thus large quantities of gas can be treated in a small reaction space. The magnesia jacket must be protected by cooling, preferably by the gases intended to be treated, which are thus preheated. In his B. P. 27790 of 1907 he describes a special apparatus for working with compressed air between suitable electrodes (Fr. P. 385193; Ger. P. 225239).

Spitzer (B. P. 22201 of 1906) passes the air into an electric arc and withdraws the gases only from the inner zone of the arc, with immediate cooling, for which purpose he describes special forms of apparatus.

Steinmetz (Amer. P. 865818) produces in a cylindrical chamber made of glass or porcelain, a long, thin light-arc by means of electrodes fixed in the top and the bottom. Outside there is an electromagnet whose widened-out poles rotate round the chamber, and thus produce a deflection of the arc in the form of a circle segment; and this also causes the air to be a very short time subjected to the heating, so that any overheating and consequent dissociation of the nitrogen oxides formed is avoided.

Hauck (Ger. P. 193518), with the intention of compensating endothermic and exothermic processes, causes the electrical formation of nitrogen oxides from N and O to take place under water or another liquid.

Gorboff and Mitkevitch (Ger. P. 196114) cool the gases coming away from the electric arc, generated in a comparatively small chamber, by means of a coil.

Grau and Russ (Amer. Ps. 884919 and 884920) withdraw the gases from the centre of the electric flame and immediately cool them, by means of an inwardly cooled tube, reaching into the centre and of the same diameter as the central zone of the flame. A cooled tubular electrode serves as the exit tube.

Neuburger (Amer. P. 850392) oxidises atmospheric nitrogen by means of electric discharges, produced by less than 120 watts in a secondary current. By employing a low watt power, he declares, the formation of nitrous vapours is avoided, and there is exclusively nitric acid formed. The same inventor's B. P. 9939 of 1907 prescribes preheating the air to at least 1000° by other means and then subjecting it to the electric arc.

Schloesing (Fr. P. 373718) absorbs the nitrous vapours, formed from air by electrical means, at temperatures of 200° to 350° by a dry fixed base, preferably lime, or the corresponding carbonate, in the shape of porous briquettes.

The Norske Aktieselskabet for Elektrokemisk Industri and Halvorsen (B. P. 3680 of 1906) absorb the nitrous gases obtained in the electric arc in a solution of SO_2 or by strong H_2SO_4, add an excess of strong sulphuric acid and oxidise by chromic acid, or a chromate, or PbO_2, or MnO_2. Thus strong nitric acid is formed which is distilled off; the remaining liquid is electrolysed, in order to recover the H_2SO_4 and the oxidising agent and hydrogen which is utilised. If a cupric salt is added, metallic copper is obtained as a by-product. The nitrous sulphuric acid can also be oxidised by ozone or H_2O_2, in which case the oxidising agent is not, of course, recovered electrolytically. Their B. P. 16885 of 1906 tends to secure better absorption of the nitrous vapours by employing solid absorbents, as lime, etc., in a pulverulent condition, contained in a series of revolving or mechanically agitated drums. Other patents of theirs are Ger. Ps. 170585, 179823, 188213.

Lee and Beyer (*Z. Elektrochem.*, 1907, p. 701) find that continuous or alternating currents have the same action in the formation of NO from atmospheric oxygen, contrary to the opinion of several inventors.

Warburg and Leithäuser (*Berl. Akad. Ber.*, 1907, p. 229; *Abstr. Amer. Chem. Soc.*, 1902, p. 2573) found that by the action of the silent discharge on atmospheric air chiefly nitrogen pentoxide is formed, besides a substance they designate by Y.

The Westdeutsche Thomasphospatwerke (Fr. Ps. 348189 and 353548), in the manufacture of nitric acid from air by means of the electric current, claim to avoid the formation of the lower nitrogen oxides by applying currents of low strength, from 200 volts downwards. This is also claimed to prevent the fusion of the electrodes. Their Ger. Ps. 157629 and 160090 prescribe special forms of apparatus for this purpose. Their Ger. P. 194326 prescribes preheating the air to 1000° before it passes through the electric arc.

Ellis (Amer. P. 1002249) blows a heated damp current of air through a zone of light-arcs, the field of which is at right angles to the direction of the current of the light-arcs, while turning these by means of magnetic fields parallel to the direction of the current.

Acker (Amer. Ps. 914100 and 914214) describes special arrangements for forming nitrogen compounds by electrolysis.

The Elektrochemische Werke, Berlin (Ger. P. 199561), obtain nitrogen peroxide from mixtures of NO and air, containing very little NO, such as are obtained by electrical processes, by cooling down to 30°. The nitrogen peroxide then precipitates in the form of a very fine fog, from which it is recovered by passing it through a very quickly revolving drum, with application of cooling. The centrifugal force throws the fine particles of N_2O_4, together with H_2O, against the wall of the drum, from which it is drawn off by suction and worked up for nitric acid. A small quantity of steam may be added for this purpose to the mixture of gases before centrifuging.

Sir William Ramsay (B. Ps. 16067 and 16068 of 1907) obtains nitrous oxides, formed by the action of electric sparks or flames on air, in a concentrated form not necessitating any evaporation of water, by absorption in magnesia (*not* in lime, which parts with the nitrogen oxides at too high a temperature), and expelling them again by heating. Other suitable absorbents for this purpose are tribasic phosphate of lime or soda, or the oxides of aluminium or iron, in the presence of water vapour; by heating to about 300° the oxides of nitrogen are expelled and collected in any usual manner, and the absorbent is then ready for use again, after being cooled and moistened.

The same inventor (B. P. 26981 of 1907), for the purpose of recovering nitrogen oxides in a state of great dilution, such as they are obtained from air by electric discharges, passes them through two heat interchangers and then through pipes, surrounded by a liquid of low temperature which may already contain some nitrogen oxides from a former operation; they partly condense then and the liquid resulting is run down a fractionating column, where it meets the products of evaporation from a vessel in which rectification takes place in the well-known manner, with the result that almost pure N escapes, and the liquid oxygen remaining behind contains all the nitric oxides present. From this liquid oxygen they are separated by another rectification.

Platsch (Ger. P. 200138) cools the products of the reaction from the light-arc by blowing in the peroxides of the alkaline earth metals in the state of powder (which possess great heat-absorbing power and do not dilute the gases); the oxygen splitting off from them increases the yield of nitrogen oxides.

Ferranti (B. Ps. 13965 of 1906; 20697 of 1907) rapidly cools the products of the combination of N+O by the electric arc. He employs a revolving annular electrode, which is hollow and cooled by water, through which the gases pass by means of a divergent pipe, which drives them against the cooling surface. Instead of an electric arc, internal combustion, or a resistance heater, or a combination of all three may be used to heat the gases.

Spitzer (B. P. 22201 of 1907; Fr. P. 383078) passes mixtures of N and O into an electric arc, and withdraws the gases from the inner zone, practically excluding those in the outer zone, through a tube in which they are rapidly cooled, to prevent dissociation of the nitrogen oxides.

A special series of efforts has been directed towards the production of nitric acid from air by *the silent electrical discharge*, *e.g.* in concentric tubes, coated with tinfoil and traversed by electric currents in opposite directions, so that in the annular space between the tubes the opposite electricities find their combination in the shape of purple streams. This silent discharge under ordinary circumstances acts much too slowly, and therefore Siemens and Halske (Ger. P. 85103) in 1894 proposed to hasten it by mixing ammonia gas to carefully dried atmospheric air, preferably after having "ozonised" it and exposing it to the silent electrical discharge, whereby solid ammonium nitrate is formed and separates in the solid form. But evidently that process also has not been found profitable in actual work.

Moscicki (B. Ps. 3583 and 27006 of 1906; Fr. P. 380614; Swiss P. 33694; Ger. P. 198240) produces NO from N in a magnetic field, in which the flame-arc revolves in a plane and the gas passes out once through the zone of heat. One of the electrodes is shaped as a hollow metallic body, powerfully cooled, with channels for the gases to pass through. In 1908 it was reported by the Neue Zürcher Zeitung (19th November) that the Aluminium-Industrie Gesellschaft was erecting works on this system in the Valais.

The same inventor (B. P. 21959 of 1908; Fr. P. 395424; Amer. P. 920610; Ger. P. 209959) blows into a revolving flame-arc, near the place of the highest heat, gases which do not take part in the reaction, such as aqueous vapour, or gases already enriched with nitrogen oxides and cooled down, introducing these through the central electrode, opposite to which is a conic prolongation of the metallic conductor, so that the gases are spread out conically.

According to his Ger. P. 230170, he places between his furnace and the absorbing-apparatus a condensing-tower, packed with distributing bodies, and fed with a mixture of sulphuric acid 60° to 61° B., and the 60-per-cent. nitric acid, obtained in the absorbing plant. The gases enter at the bottom of the tower, and are quickly saturated with nitric acid. This acid is mostly condensed in a second tower, in a concentrated form; the remainder is retained in a third tower, fed with dilute nitric acid. The dilute sulphuric acid, collecting at the bottom of the condensing tower, is concentrated to 60° to 61° B. in leaden pans, which are heated by the gases on their way from the electric furnace to the condensing tower. A further modification is described in his Ger. P. 236882.

Naville, C. E. Guye, and P. A. Guye (B. P. 21338 of 1906; Fr. P. 361827) cause the electric arc to revolve by means of a rotating field, the gases being introduced by one of the electrodes, which is hollow; the other electrode has the shape of a disc with projecting margin, or of a cone. The gases are absorbed in concentrated sulphuric acid, the nitric acid formed is distilled off, and the lower nitrogen oxides are further oxidised. Their Fr. P. 385569 prescribes absorbing the gases at first only partly, then desiccating by refrigeration or by dry calcium nitrate, and then oxidising the NO further. Fr. P. 385605; B. P. 6366 of 1908 describes a series of towers and chambers, in which short periods of absorption alternate with periods of oxidation.

The same inventors, in Ger. P. 210821, produce a double movement of the flame-arc, obtained by an alternating current in a revolving magnetic field, fed by an alternating current of less periods. This double movement is very favourable for chemical reactions, such as the oxidation of N. They dry the gaseous products and oxidise them as much as possible before absorbing them.

According to Guye's report (*Z. Elektrochem.*, 1910, p. 848) the arc, with a current of 50 kw., has a length of 4 m.; with 200 to 250 kw., 12 m.; with 500 kw., 20 m. The condensation of nitric acid is brought about by the expansion of the furnace gases, compressed to 5 atm., and nitric acid of 95 per cent. can be obtained.

The Neubabelsberg Zentralstelle fur wissenchaftlichtechnische Untersuchungen (Ger. P. 211196) produce the flame-arc by a perforated tube, surrounded by a vessel into which the air, to be oxidised, enters, and then passes into the arc through the perforations of the inner tube. Thus the arc is never cooled down too much; the heat required for heating up the air is supplied by that of the flame-arc. The tube surrounding this is best composed of rings, between which there are gaps for the air to go through.

The Elektrochemische Werke, Berlin (Ger. P. 206948), produce between two concentric tubular conductors a light-arc with a tension of 5000 to 10,000 volts, which turns round by a whirling movement of the air, more quickly at the outer than at the inner ring, so that the light-arc is spread out round the inner ring in a spiral form, and fills this space almost entirely. The air enters in a screw movement through the flame, and in consequence of this mixes at once with the air already cooled at the walls of the vessel, so that the newly formed nitrous gases are hardly at all decomposed. Their Ger. P. appl. C13895 describes for this purpose a plan for producing travelling flame-arcs.

Kunheim & Co. (Ger. P. 212881) construct their apparatus of fireclay. It is a cylinder with a conical upper part, open at the top, where the air enters, containing two electrodes made of iron T-pieces. The current has a tension of 3000 volts. The air-valve is regulated in such manner that the light-arc is drawn down about half-way into the vessel, where it burns quietly and completely fills the space.

Vender (B. P. 18280 of 1908) asserts that hot gases, obtained by the combustion of atmospheric nitrogen by an electric arc, denitrate nitrosulphuric acid recovered from the waste acid of nitrating processes (for glycerine, cellulose, benzol, etc.) much better than heated air, and that thus perfectly clear sulphuric acid of 98 per cent. can be obtained. This he attributes to the NO contained in those gases, which thereby is also more easily transformed to higher nitrogen oxides. The process is carried out by means of two sets of tower apparatus The hot gases produced by the combustion of air heat the first tower outside and pass into the interior of the second tower at the bottom, while the waste acid from those nitrating processes runs down. At the bottom of this tower concentrated sulphuric acid runs out; on the top nitrous gases come out which, when treated in an ordinary condensing apparatus, yield nitric acid of 60 per cent., and this, together with the concentrated sulphuric acid obtained at the bottom, is made to feed the first tower. From this tower escape vapours which on condensation yield nitric acid of 98 per cent., and at its bottom sulphuric acid of 75 per cent. runs out which is fed into the second tower. By this means, the inventor asserts, nitric acid can be manufactured by synthesis in the industry of nitrating processes, even in such cases where the process in question by itself would be too expensive; and the consumption of sulphuric acid is confined to losses by leakages.

Haber and Koenig (B. P. 15490 of 1908; Ger. P. 210166; Fr. P. 392670; Amer. P. 938316) treat mixtures of N and O for the production of nitrogen oxides by the electric arc at a low pressure in spaces of such shape that they are almost entirely filled by the electric arc and that this arc is sufficiently cooled. Thereby from a mixture of equal volumes of O and N, gases containing 13½ to 14 per cent. NO, and from atmospheric air gases with 9½ to 10 per cent. NO are obtained. The light-arc is produced in long cylindrical vessels, in case of necessity cooled outside. The electric discharge can be produced by temporary evacuation; when the arc is once formed, the pressure may be allowed to rise again. Electrodes made of electrolytes have the advantage of producing less dust than metallic electrodes. The yields mentioned above were obtained by means of a water-cooled quartz cylinder, through which the air or the mixture of O and N passed at a velocity of only 0·2 m. per second, and at a pressure of only 90 mm. mercury. The pressures may vary between 80 and 200 mm. Morden (*J. Soc. Chem. Ind*., 1909, p. 520) continued his work by laboratory investigations. The best yield he obtained at 400 mm. pressure and with low voltage, viz., 92 g. HNO_3 per kilowatt hour. Haber, in *Z. angew. Chem.*, 1910, pp. 684-689, reviews the present state of the recovery of nitric acid from air. Assuming the cost price of atmospheric nitrogen (free from oxygen) = 0·03 mark (M) prokg., nitrogen in nitrate = 1·20 M. and nitrogen in ammonium sulphate = 1·05 M, the value of nitrogen for assimilation may be taken as exceeding 1 M. This, at a consumption per annum of 2,000,000 tons nitrate = 315,000 tons N, and 700,000 tons ammonium sulphate = 140,000 tons N, means a total consumption of 455,000 tons N, or an assimilation value of 525,000,000 M. In order to render the utilisation of atmospheric N successful, 1st, the electrical energy employed must attain a considerable amount; 2nd, the concentration of the nitrogen oxides must be somewhat considerable; and 3rd, the electrical discharge apparatus must admit of getting through a large quantity of energy, that is of air, with a simple apparatus. Only cheap water-power can compete here. The best conducted plant, according to Schönherr's process, yields from 1 to 2·25 per cent. NO. The discovery of Haber and Koenig, according to which the formation of NO is not a purely thermic reaction, but that in a cooled light-arc concentrations up to 90 per cent. and upwards can be obtained, promises a thorough revolution in this field.

The Swedish Nitric Syndicate (Ger. P. 233031) utilise the gases coming from the electric furnace, where N and O are combined, for concentrating nitric acid by direct contact.

Limb (Fr. P. 403536) describes for the treatment of atmospheric nitrogen the production of an arc by means of a rotating magnetic field, obtained by the use of polyphase currents.

Sénez and Giniès (Fr. P. 414726) describe an electric furnace for the same purpose.

Pawlikowski (Ger. P. 225195) describes an apparatus for quickly compressing the gases for that purpose.

H. Howard (Amer. P. 952248) compresses the gases and allows them to expand quickly, turning the heat into mechanical work.

Presser (B. P. 7319 of 1910) passes a mixture of N and O through a tube heated to a high temperature by an electric current. The tube is provided with many small apertures through which the nitrogen oxides formed escape into the surrounding space, which is kept under diminished pressure, so that the expansion of the gases causes the temperature to fall about 500°.

J. Price (B. P. 10164 of 1909) fortifies the gases, derived from air by electrical methods, by adding oxygen obtained by the barium process, and with such a mixture he feeds an oxy-hydrogen flame, to assist in the combination of N and O. The gases are passed into water or bases and are separated from the water by converting this into superheated steam, which is then used in the barium process.

Kaiser (B. Ps. 12229 of 1909; 12220 and 20325 of 1910; Ger. P. 230042; Fr. P. 415976; Amer. P. 984925) produces an alternating current of high tension (25,000 volts) within a tube, and forces a current of air, previously heated to 300° to 400°, through it, at the same time drawing in small quantities of gaseous ammonia, which greatly promotes the yield of nitrogen oxides. The mixed gases then pass through a fine platinum net, kept in the forepart of the tube. Without the addition of NH_3 the yield is only 2½ per cent. NO; with NH_3, it increases to 6 per cent. (*cf.* the Siemens process of 1894).

The Dynamite A. G. vorm. Nobel (Ger. P. 228849) describe the formation of a steadily burning light-arc in a non-conducting tube, outside of which there is all along its length a number of oppositely arranged revolving magnetic fields, so that the air within the tube is alternately heated and cooled. Their Ger. P. 223336 describes an arrangement, for the same purpose, consisting of a vessel within which there are rings of airtuyeres, reaching nearly as far as the light-arc, from which that arc receives an air-blast from all sides. Their B. Ps. 24607 of 1910 and 9682 of 1911, taken together with D. Cross, bear on the same matter.

Timar (Ger. P. 223887; Fr. P. 412227), in order to attain a very high temperature and rapid cooling of the reaction products, produces the heating in a tube made of magnesia, from which the gaseous mixture issues in one or more quickly expanding jets. That body is interposed in the electric circuit, and is thereby brought to the requisite high temperature.

Du Pont's apparatus (Amer. Ps. 943661, 948372, and 950703) also aims at rapid cooling. The perpendicular quartz tube holding the electrodes is surrounded by a silica tube, and cold water is run through the annular space between them, while a revolving magnetic field keeps the light-arc in constant circulation. The air enters into the quartz tube under a pressure of 50 atm. at the bottom and comes out at the top. His Amer. P. 946361 describes a "container," *i.e.*, an electrical non-conductor, in a cooling-medium, within which the arc is longitudinally produced; externally a series of rotary magnetic fields extends between the electrodes.

The Chemische Fabrik Griesheim-Elektron (Ger. P. 193367) forms electrodes of fused magnetic iron oxide; the molten mass is allowed to cool in the mould, until a solid, cylindrical shell is formed; the remaining fused oxides are run out, and a solid or hollow metallic core is put in.

The same firm (Ger. P. 228422) produces horizontal light-arcs and quickly removes the products of reaction by introducing all along the arc gas from a system of shutter-like slits, so that the arc cannot rise upwards, but is pressed downwards by the inrushing gases and blown against the (adjustable) electrode. Their Ger. P. 234591 describes several special arrangements of the aforesaid slits, and other improvements of the apparatus; so does their Ger. P. 235429. The B. P. is 5934 of 1910; Amer. P. 981727; Fr. P. 412262; Belg. P. 204187; Ital. P. 321111; Hung. P 50856; Swiss P. 51272; Canad. P. 125696, etc., etc.

Albihn (Ger. P. 228755), in order to start the way for the lines of force, arranges the electrodes in the shape of two concentric rings; this allows the construction of very small furnaces of high capacity.

Le Nitrogène S. A., Geneva (Ger. P. 228423; Fr. P. 404230), prevent the extinction of the light-arc, which is easily brought about by the strong movement of the gases, by protecting the head of the electrodes by a fire-proof screen, or placing them in hollow spaces in the walls. In the case of a continuous current, the cathode only need be protected.

The same firm (Fr. P. 404720) dries the gases before or after the formation of nitrogen oxides by the electric arc, and produces nitric acid of 65 per cent. by absorbing the nitrogen oxides from these dried gases in water.

J. L. Roberts (Amer. P. 902607) produces NO from elementary N and O by passing them upwards in a tube in which an electric arc is formed containing chromium, or chromium and iron.

Binaghi (Ital. P. 92840) decomposes sea-water by the electric current and passes through the solution air which has passed through several light-arcs, by which means sodium nitrate is formed.

Brunet, Badin, and the Compagnie d'Alais (Fr. P. 402012; B. Ps. 16224 and 16225 of 1909; Ger. P. 237796), for the purpose of improving the yield of nitrogen oxides, maintain the temperature of the electric arc constant, by using an alternating current of 200 to 1000 periods per second, and quickly cool the products by contact with a liquid. The electrodes are arranged to form an upright fork in a chamber through which a regulated supply of air is passed from below; a succession of expanding arcs travels up, and is immediately extinguished on entering a wider chamber above by jets of pulverised liquid, which absorbs the nitrogen oxides formed. An addition to this patent describes the ultimate passing of the gases through an apparatus in which they are subjected to the silent electric discharge, so as to oxidise all nitrous compounds to nitric acids.

The processes of H. and G. Pauling (*Salpetersäure-Industrie-Gesellschaft* (*Gelsenkirchen*), at Cologne) have during the last years roused great attention. Their patents for the manufacture of nitrogen oxides from air by electric methods are:—B. Ps. 5540 of 1904; 7869, 7870, 7871, 8452, 18599 of 1906; 18901 of 1907; 22037 of 1909; 9884 and 22319 of 1910; 14121 and 14122 of 1911. Amer. Ps. 807491; 877446; 877447; 877448; 896144; 873898; 991356; 991357; 993868; 999586; 999587. Austr. Ps. 27726; 31485; 31846; 49035; 34029. Ger. Ps. 180691; 182849; 184958; 186454; 187367; 193366; 193402; 196112; 196829; 198241; 202763; 203747; 205018; 205464; 211919; 213710; 216090; 231584; 235299. Ger. P. appl. S30557; 31188; 31189; 31716; 26008; 26009.

We shall describe their processes principally according to the description given by Russ, in *Oesterr. Chem. Zeit.*, 1909, pp. 142 *et seq.*, of the factory erected at Patsch, near Innsbruck, and driven by water-power of 15,000 h.p. Two other factories, of 10,000 h.p. each, are in course of erection in the South of France and in Northern Italy. I shall also make use of special information received from the inventors.

The electric light-arc furnace consists of two parallel shafts, lined with fire-bricks, in each of which a flame is burning. The water-cooled electrodes are bent in the shape of the well-known lightning-conductors, designated in German as "Horner-Blitzableiter." The flame-arc, lighted in the narrowest part of the conductor, rushes upwards, owing to the upward tendency of the hot gases, and tears off at every half-period of the alternating current, a new flame being always lighted at the narrowest (and lowest) part. If a current of air of great velocity is blown in between the electrodes of such a lightning-conductor, the arc is still further driven out, and arcs of considerable length are thus produced, consuming 200 kw. and more.

In order to obtain flames of high electric energy at a comparatively small tension, and yet to blow in large quantities of air, a special lighting-arrangement (Ger. P. 198241) is employed, of which Fig. 41 is a sketch. The main electrodes *a*, at the place of the least distance from each other, have a narrow slit through which pass horizontally movable "Zündschneiden," *i.e.*, strips of copper, *b*, which are placed within the distance required for producing a quietly burning flame, by means of the contrivance *d*, moved by hand and connected with the "Zündschneide" by an insulating intermediate piece *c*. As these copper strips are very thin, they do not disturb the motion of the air which rushes out of the tuyere *e*, in a width of 40 mm. at the narrowest place. The air is preferably preheated. The tuyere *e* is shaped in such manner that the current of air, on issuing from it, takes a divergent course and washes the electrodes all along their length. The flames are very easily regulated; they burn most quietly, and are about a metre long. The electrodes are made of iron, cooled by water, and stand on the average two hundred working-hours. The "Zundschneiden" are more quickly used, and must be put at the proper distance from time to time.

As the flame is lighted at every half-period, there is, *e.g.* with alternating currents of 50 periods, a flame-band formed each $\frac{1}{100}$ second; this is drawn out by the air current and tears off at a definite distance of the electrodes. Then follows the next flame-band, which is again drawn out and torn off, and so forth. The quick succession of these flame-bands produces the impression of a continuous flame of extraordinary light-power.

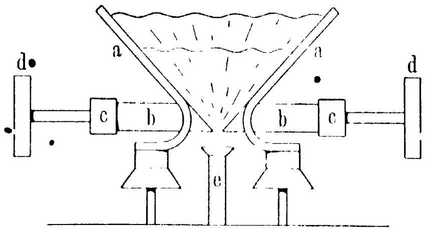
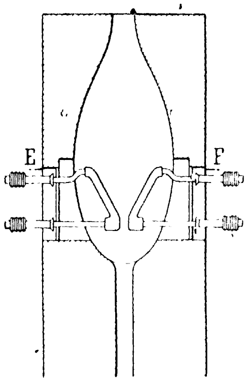


FIG. 41.

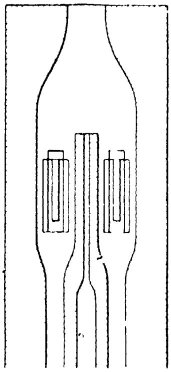
The ignition takes place with a tension considerably greater than the working-tension, so that there is only a slight differentiation of phases and the flame burns quietly. By applying the arrangement Ger. P's. 193366 and 213710 any desired number of flames can be made to burn parallel or one behind the other, so that the power developed by a generator of any amount of force can be electrically utilised. It is therefore unnecessary to build special generators for working the furnaces, which is required for constantly burning flames; but the furnaces can be worked from any central power generator, with full utilisation of the energy at disposal. Owing to this easy putting in and out of the furnaces, a central lighting-station in combination with a furnace plant can be utilised to the extent of 96 per cent. on the average of twelve months. At present (1911) there are furnaces at work which consume upwards of

1200 kw. The yield obtained is from 60 to 65 g. HNO_3 per kilowatt hour. Hence the power of the generator is better utilised than with standing flames of a total yield of only 0·35 to 0·4.

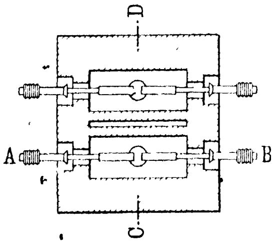
The flame-gases, leaving the furnace at a temperature of about 1200° must first be rapidly *cooled*. This takes place by means of "circulating-air," laterally introduced into the upper part of the flame-gases and specially cooled (Ger. Ps. 193402, 202763, 203747). This "circulating-air" consists of part of the cooled reaction-gases, branched off before the furnace-gases enter the condensing-plant. Thereby concentrations of 1·5 per cent. NO by volume are obtained on the large scale.



Cut A -B
FIG. 42.



Cut C—D
FIG. 43.



Cut E—F
FIG. 44.

As stated above, two light-arcs are always burning in a common furnace, as they are shown in Figs. 42, 43, 44, which is driven with a performance of 400 kw. per furnace at a current-tension of about 4000 volts; 600 cbm. of air per hour pass through each furnace, not counting the "circulating-air."

In the Innsbruck factory twenty-four such furnaces are at work, consuming 15,000 h.p. One man can attend upon six furnaces. Two other factories, with 10,000 h.p. each, are in course of erection in the South of France and in Northern Italy, and another at Höhn, near Wiesbaden, for 10,000 h.p. (According to *Chem. Zeit. Rep.*, 1911, p. 475, the Pauling process was working at Roche de Rame with 20,000 h.p. water-power. The temperature was kept at 600°, and per kilowatt-hour 60 g. HNO_3 was formed.)

The heat of the gases, leaving the furnace at 700° to 800° C., is utilised for preheating the blast-air, for contracting the nitric acid and for evaporating the solution of sodium nitrite. The gases then enter the condensing-plant, consisting of stoneware pipes and towers, where they meet a counter-current of water, and produce nitric acid of 35 up to 50 per cent., which is usually further concentrated to 60 per cent. by the heat of the furnace-gases; it is possible to go up to 98 per cent. The nitrogen oxides, remaining in the gases after the condensation of the nitric acid, are completely utilised for the manufacture of sodium nitrite.

The following notes refer to some improvements protected by the same firm.

The Salpetersaure-Industrie-Gesellschaft, Gelsenkirchen (Ger. P. 182849), obtains from atmospheric air on one side mixtures of O and N very rich in oxygen, on the other such mixtures very rich in nitrogen, by applying the principle of counter-current to the well-known capacity of water or alcohol to dissolve under equal circumstances more O than N, or *vice versâ.*

Their Ger. P. 205018 prescribes cooling the nitrous gases obtained by their method by artificial cold below 0°, whereby acid of 60 per cent. is obtained. Ger. P. 213710 describes placing several flame arcs in series. Ger. P. 216090 another contrivance for this purpose; also, B. P. 9884 of 1910.

Their B. P. 22319 of 1910 (with Pauling) prescribes heating the mixture of N and O to a high temperature, and causing it to expand without fall of temperature. It is introduced into a chamber, where there is a vacuum of 400 mm. mercury; this chamber is heated to maintain the temperature during the expansion of the gases, which are subsequently cooled. By the expansion the reactivity is so reduced that the proportion of nitrous oxides produced at the highest temperature is nearly maintained during the cooling. The German patent for this process is No. 235299.

In their Amer. P. 807491 it is claimed to convert atmospheric nitrogen quantitatively into nitric acid in two phases: first, treating the air with spark discharges, and thereupon oxidising the nitrous oxides formed by exposing them to ozone, formed by dark electric discharges. By means of absorption in water, or previous treatment with steam, ultimately nitric acid is obtained in a more or less concentrated form.

Amer. P. 991357 provides for expanding the compressed air after its treatment in the arc-space, so that it is cooled down and the decomposition of the nitrogen oxide formed is prevented. A special furnace for this purpose is described in Pauling's Amer. P. 999587, and in Amer. P. 999586 of the Salpetersaure-Industrie-Gesellschaft (Ger. P. 231584). Pauling's B. Ps. 14121 and 14122 of 1911 describe a tower for absorbing the nitrous gases produced by his processes by sulphuric acid, after having been first dried in a similar tower. The French patents are Nos. 430111 and 430112; the Ger. P. No. 244840 and 246712.

Processes of Birkeland and Eyde.

Among the most successful attempts at oxidising atmospheric nitrogen are those of Professor Birkeland, in Kristiania, and Eyde. Witt (*Chem. Ind.*, 1905, pp. 703 *et seq.*) drew special attention to their process, and this became still better known by a paper read by Birkeland in London to the Faraday Society in 1906 (*Trans. Far. Soc.*, vol. ii., September 1906). An illustrated description of that process and the Notodden factories is given by De la Vallée Poussin, 1910, Lyon, chez Rey and Cie. The principal element in their process is the production of a peculiar form of high-tension flame, never before employed in technics, but since then proved to be a powerful technical aid in various chemical reactions. Two pointed copper electrodes, attached to a high-tension alternator, are placed equatorially between the poles of a powerful electro-magnet, in such a way that the terminals of the electrodes are in the middle of a magnetic field. Thereby an electric disc flame is formed, such as is shown diagrammatically in Fig. 45; the flame here shown, which represents about 250 h.p., is established between water-cooled electrodes made of copper tubing of 15 mm. diameter.

The working potential employed here is 5000 volts; the current is an alternating current of 50 periods per second, and the terminals of the electrodes are at a fixed distance of about 8 mm. from one another. Even with flames of 750 kw. at 5000 volts, the same kind of electrodes can be employed, and here, too, the distance between the terminals of the electrodes is not more than about 1 cm. By the cooling of the electrodes with water, about 7·5 per cent. of the electric energy engaged between the electrodes is removed by the water as heat.

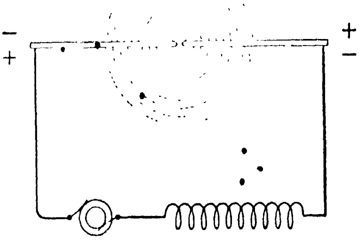


FIG. 45.

The formation of these disc flames may be explained as follows: at the terminals of the closely adjacent electrodes, a short arc is formed, thus establishing an easily movable and ductile current-conductor in a strong and extensive magnetic field, *i.e.*, from 4000 to 5000 lines of magnetic force per square centimetre in the centre. The arc thus formed then moves in a direction perpendicular to the lines of force, at first with an enormous velocity, which subsequently diminishes; and the extremities of the arc retire from the terminals of the electrodes. While the length of the arc increases, its electrical resistance also increases, so that the tension is increased, until it becomes sufficient to create a new arc at the points of the electrodes. The resistance of this short arc is very small, and the tension of the electrodes therefore sinks suddenly, with the consequence that the outer long arc is extinguished. It is assumed that, while this is taking place, the strength of the current is regulated by an inductive resistance in series with the flame.

In an alternating current (Fig. 45) all the arcs with a positive direction of current run one way, while all with a negative direction run the opposite way, presupposing the magnetising being effected by direct currents. In this way a complete, luminous, circular disc is presented to the eye. The flame extends farther along the positive electrode than along the negative.

The extremities of an arc may sometimes appear like glowing spots upon the back of the electrode. The spots of light on the positive electrode are small, and lie exceedingly close to one another; while those on the negative electrode are larger, and the distance between them is greater. The reason of the appearance of these spots of light is that the arcs, so to speak, melt or solder themselves to the electrodes, so that the electric force can only make the extremities of the arcs move along the electrodes in tiny leaps. It is evident from the curvature of the arcs that they cling more closely to the negative than to the positive electrode; and, therefore, the flame extends farther along the positive electrode than along the negative.

When the flame is burning it emits a loud noise, from which alone an impression may be obtained of the number of arcs formed per second in the flame. By the aid of an oscillograph, the tension curve for the electrodes and the current curve can easily be drawn. (In the original several such curves are reproduced.)

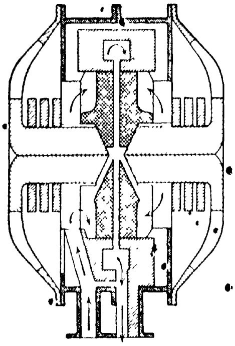


FIG. 46.

The flame here described was, for the purpose of producing nitric acid from air, enclosed in a special furnace, with a metal casing lined with fire-brick. The more recent form of this furnace is shown in Fig. 46. The fire-chamber is only 5 to 15 cm. wide, in the direction of the lines of force, made partly of perforated fire-brick, air being supplied in an evenly distributed supply through the walls. The system of magnets is composed of two powerful electro-magnets, their extremities turned in towards the fire-chamber. The magnetic circuit is closed, either as in a horse-shoe magnet, or through the cast-steel casing of the furnace. The air is driven into the central region on both sides of the flame by gentle pressure from a Root's blower; and after passing in a radial direction arrives at a peripheral channel, whence it is conducted away. The horizontal electrodes are made of copper tubing, 15 mm. in diameter, whose terminals are within about 1 cm. of one another, and are cooled by water in circulation which keeps them from fusing. The electrodes are exchanged and repaired after being in use for about three hundred hours, the exchange itself taking about fifteen minutes to accomplish.

At the factory at Notodden, in Norway, where this process (after having been tried elsewhere on an experimental scale) has been carried out on a large scale, there were in 1906 three such furnaces, at 500 kw. each, in full activity. They burn extremely steadily, with a variation in energy of only 2 to 3 per cent., although the electrodes have no automatic regulation. It has happened that a furnace has burned for forty hours without being attended to. The furnaces themselves give notice of anything going wrong, for the flame begins to roar, in ample time to allow of an adjustment before the flame is extinguished.

The fire-brick lining stands very well, in spite of the enormously high temperature of the disc flame, as the temperature on the walls does not rise above 700° during normal working, owing to the cooling effect of the current of air. An estimate of two or three renewals of the lining per annum has proved too high.

In the new manufactory at Notodden,[1] which obtains 30,000 h.p. from a waterfall, 5 km. distant, the furnaces will be up to 750 kw. under normal conditions, and during flood-tide up to 850 kw. With a working-tension of 5000 volts, the power factor for these furnaces will be about 0·75. The cost of a furnace, including induction resistance, is £1000, fully complete and capable of being attached to an ordinary alternating-current with a tension of 5000 volts. They therefore cost only £1 per kw., which is surprisingly low; but in the future the cost will be even less, as they would be made much larger. Furnaces of 2000 kw. would cost only about £1100 to £1210. I hear from Prof. Birkeland that in 1911 furnaces of 3000 to 4000 kw. were used, and they were to go as far as 6000 kw.

The nitric oxide fumes, formed in the furnaces and conducted away with the hot gases, fix, after cooling, more oxygen and form nitrogen peroxide which, on treatment with water, yields nitric acid. The volume of air thus treated in the three furnaces in 1906 was 75,000 l. per minute, and contained afterwards 1 per cent. NO. This rarefaction, of course, causes difficulties.

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[1] Other factories are placed at Svelgfos, Lienfos, Rjukan, and Saaheim.

The gases, coming from the furnace with a temperature of 600° to 700°, first pass through a steam-boiler, the steam of which is utilised in the manufacture of the ultimate product, calcium nitrate. (In the new plant the gases are directly passed through the evaporation-tank, which produces such a saving of heat that the employment of coal may presumably be avoided.)

After leaving the steam-boiler, the temperature of the gases is 200°, and they are now further cooled down to 50° in a cooling-apparatus, in order to be more easily absorbed by water. The gases then enter two large oxidising-chambers, with acid-proof lining, where the NO is converted into nitric peroxide; this is then converted into nitric acid, in two series of stone towers, 2 x 2 x 10 m. inside. Each series consists of five towers, two of granite, two of sandstone, filled with pieces of quartz, over which water is flowing and nitric acid is formed; the fifth tower is packed with bricks, over which milk of lime is run down and absorbs the last nitrous gases, with formation of calcium nitrate and nitrite. The first tower yields nitric acid of 50 per cent., the second about 25 per cent., the third 15 per cent., and the fourth 5 per cent. The liquid from the fourth tower is raised by compressed air to the top of the third, that from the third to the second, and that from the second to the first, thus gradually increasing in concentration up to 50 per cent.; it is then conducted into a series of open granite stone tanks. Some of it is employed to decompose the calcium nitrite formed in the fifth tower; the N_2O_3 driven out is carried back to the towers.

The solution of calcium nitrate thus obtained, together with the nitric acid stored-up, is converted in a series of granite tanks by means of limestone into a neutral solution of calcium nitrate. This solution is either evaporated in iron vessels to a boiling-point of 145°, answering to a concentration of 75 to 80 per cent. calcium nitrate or 13·5 per cent. N., which is run into iron drums of about 200 l. capacity where it congeals, and in that form goes into the market; or else it is evaporated only to a boiling-point of 120° and allowed to crystallise. The calcium nitrate crystallising out has the composition $Ca(NO_3)_2+4H_2O$ and is hygroscopic. It is used as a fertiliser, and is rendered more fit for that purpose by converting it, according to a suggestion from Dr R. Messel, into basic nitrate, which keeps dry and can be scattered with a sowing-machine. It is quite as good a fertiliser as the natural saltpetre, and on sandy soil, which is deficient in lime, even superior to it.

The cost of production in the factory erected at Notodden in 1906 was estimated at £4 per ton of calcium nitrate, containing 13·2 per cent. N, the selling price at £8, as reckoned from the selling price then ruling for combined nitrogen = £60.

Eyde, in *J. Soc. Arts*, 1909, pp. 568, 574 (*J. Soc. Chem. Ind*, 1909, p. 1214), also describes the process as then carried out at Notodden, where at that time 40,000 to 45,000 h.p. were used for it.

In 1910 there were at Notodden thirty-two furnaces, going with 800 to 850 kw., and altogether consuming 25,000 to 26,000 kw., say, 34,000 to 35,000 h.p. The air entered the furnaces at the rate of 1000 cbm. per second. Both the Birkeland-Eyde and the Schonherr process (see below) were in operation.

In 1911 Scott Hansen, in a lecture before the Faraday Society, reports that 180,000 h.p. were to be employed for this manufacture at Notodden, in which the Badische Soda- und Anilinfabrik has a considerable share. He very fully describes the various establishments, already erected or planned, for utilising the Norwegian water-powers in the manufacture of chemicals, in the first instance of nitric acid from air (*Chem. Trade J.*, 1911, xlviii. pp. 454-455).

According to *Z. angew. Chem.*, 1911, p. 1263, the natural gas, issuing at Kissarvas (Hungary), is to be utilised for manufacturing nitrate fertilisers from air, by the process Birkeland-Eyde and Schönherr, to the extent of 9400 tons calcium nitrate and 2500 tons sodium nitrate.

Ammonium nitrate is also to be manufactured on a large scale at Notodden, to the extent of 15 tons per day. A description of the installation for that purpose is made by Bühler in *Chem. Ind.*, 1911, pp. 210-212.

The patents of Birkeland and Eyde for their nitric acid process are as follows. In Norway fifty-three various patents were taken out for it, and most of them applied for in all other countries. The principal foreign patents are:—B. Ps. 20049 of 1903; 20003, 28613, and 28614 of 1904; 3525 of 1905; 16885 of 1907; 6265 of 1908. Ger. Ps. 170585; 179825; 179882; 214445. Amer. Ps. 772862; 775123; 906682. Fr. P. 335692.

Properties and Analysis of Norwegian Nitre (*Norge Salpetre*).—According to Hals (*Chem. Zeit.*, 1911, p. 1130) that article, which for commercial purposes is partly freed from its water of crystallisation, is much more hygroscopical than Chilian nitrate of soda. This property may sometimes interfere with its use as a fertiliser.

The analytical methods for Norwegian nitre (lime, nitrogen, etc.) are treated by Dinslage in *Chem. Zeit.*, 1911, p. 1045, and by Stutzer and Guye (*ibid.*, p. 891). The latter chemists employ by preference the "Nitron" method, described by Busch in *Berl. Ber.*, 1905, p. 861, and 1906, p. 1401; and in Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i. p. 311.

Statistical.—The exports of Norwegian air-saltpetre (Norge Salpetre), according to the Central Statistical Bureau at Kristiania (quoted in *Journ. Indust. and Engin. Chem.*, 1911, p. 948), have been as follows (in tons):—

Country to which exported.	1908.	1909.	1910.
Denmark	538	256	392
Germany	3841	4803	4791
Holland	1270	1149	1687
Belgium	32	136	363
Great Britain	619	2530	4900
France	671	152	683
Other countries	81	340	694
Total	7052	9366	13530

According to *Chem. Trade J.*, 1911, vol. xlix. p. 632, there was further exported from Notodden:—

	1909.	1910.
Sodium nitrite	2577	502 tons.
Sodium nitrate	3200	1074 "

According to *Chem. Ind.*, 1912, p. 69, the exportation from Norway in the year 1910 amounted to 13,531 tons calcium nitrate, 3200 tons sodium nitrite, and 1074 tons sodium nitrate. In the meantime also the manufacture of ammonium nitrate has taken a vigorous share.

Processes of the Badische Anilin- und Sodafabrik (*Schonherr*).

Among the most successful inventions for the productions of nitric acid from air are those made by the chemists of the Badische Anilin- und Sodafabrik at Ludwigshafen. We shall in this place report upon them in the first instance from the publications, made by two of the gentlemen connected with that firm, viz., Dr Schonherr in *Electrotechnische Zeitschrift*, 1909, parts 16 and 17 (more briefly in *Z. angew. Chem.*, 1908, pp. 1633 *et seq.*), and Professor Bernthsen, *ibid.*, 1909, pp. 1167 *et seq.*

Schonherr justly points out that the formation of nitrous gases from air by the action of high temperatures under ordinary circumstances does not take place to a sufficient extent to be noticeable, but that another condition must undoubtedly be observed, if considerable quantities of nitric acid are to be obtained, viz., the rapid cooling of the highly heated air. The formation of a gramme-molecule = 30 g. NO from $10\ \mathrm{O} + 14\ \mathrm{N}$ absorbs 21,600 calories. According to a general law this formation increases with the time and the temperature, but for each temperature it cannot be driven, by ever so much prolonged heating, beyond a certain point at which an equilibrium is reached, because at that point in the unity of time just as much NO is decomposed into $\mathrm{N} + \mathrm{O}$ as is newly formed by the opposite reaction. According to Nernst the formation of NO from atmospheric goes on at

Degrees.	
1500 (abs. temp.)	up to 0·1 per cent.
1928 „	„ 0·5 „
2002 „	„ 1·0 „
2403 „	„ 1·5 „
2571 „	„ 2 „
2854 „	„ 3 „
3193 „	„ 4 „
3327 „	„ 5 „

Hence, in every case a very large quantity of air must be heated without furnishing NO. Calculation shows, for instance, that at 1928° five times as much heat must be expended as at 3327°, in order to yield the same weight of NO. From this it follows that only such processes have a prospect of economical working in which the air is very highly heated. By means of the electric light-arc temperatures of 3000° can be obtained. But it is impossible to produce NO in the corresponding concentration, since an increase of temperature increases not only the concentration of NO, but also the velocity, both of its formation and of its decomposition, for at the point of equilibrium just as much of the substance in question is decomposed as is newly formed within the same time. The velocity of decomposition at 3000° is about ten million times greater than at 1900°. Hence the cooling of the products of the reaction must take place with enormous rapidity, and the practical yield of any process will principally depend upon the more or less fortunate application of this principle. Up to now the greatest success in this line has been attained by applying an excess of air, which indeed takes place in most technical processes for this object, intentionally or unintentionally; all other cooling agents act too slowly. The dilution by this excess of air also acts favourably for preserving the once-formed NO, because the velocity of its decomposition also falls rapidly with its concentration.

To be sure, already in 1906 Warburg pointed out that other than purely thermic effects may take place when treating air in the electric light-arc, and Haber and Koenig have in fact obtained such concentrations of NO as are impossible if only the purely thermodynamic conditions of equilibrium were prevailing. In a partial vacuum, at 100 mm. mercurial pressure, they obtained NO concentrations up to 10 per cent. But Schönherr points out that in all technically applied processes for heating air by light-arcs, with very high intensities of current and pressures near the normal, those special effects, observed by Haber with more diffuse discharges, recede into the background, and the purely thermical interpretation of the action may be applied also to the electrical heating.

The concentration of the product depends also upon the proportion of the quantities in which the reacting substances are employed; as Schönherr calculates, a mixture of equal volumes of N and O would yield 20 per cent. more NO than

4 vol. N + 1 vol. O, *i.e.*, atmospheric air; but up to the present the employment of mixtures containing such an excess of oxygen would cost too much.

After referring to the unsuccessful attempts of the Atmospheric Products Co. (*suprà*, p. 216) and many other inventors, and to the success attained by Birkeland and Eyde's magnetic furnace (*suprà*, p. 232), Schonherr speaks of the work done at the Ludwigshafen factory, on the encouragement given by Dr von Brunck, a little before 1900. In 1905, Schonherr succeeded in finding a method for the combustion of nitrogen, still simpler than the magnetic furnace, and he was assisted in working it out by Hessberger. Whereas up to then it was considered advantageous to produce a series of very rapidly moving light-arcs (as in the Birkeland-Eyde furnace), the process of the Badische (*i.e.* Schönherr's) employs a very quietly burning stable light-arc of very high current density. This light-arc is of a peculiar kind. Schönherr had observed that it is quite impossible to make large quantities of air traverse *through* a light-arc, as attempted by many inventors. In this case only a very small quantity of air gets into the area of electric discharges, and very small concentrations are obtained. High concentrations are obtained by carrying the air close to a quietly burning light-arc. But this is not so easy as it seems, for a freely burning light-arc of some length is extinguished very easily, and this happens all the more as very great velocities of air must be employed in order to utilise the energy. Moreover, the pulsations of the alternating current (and no other currents can be thought of nowadays), its swelling from zero to a maximum, its reversion and flowing in the opposite direction, cause such violent disturbances in a regulated supply of air that it would appear impossible to resolve that task satisfactorily. But this can be brought about after all by carrying the air along the light-arc not in a straight line, but in a screw-motion. The alternating-current arc then burns as quietly as a candle, and can be enclosed in a pretty narrow tube without touching its walls. In practice the factory employs exclusively light-arcs, burning in the centre of a vortex. In the interior of the tube, insulated from this, an electrode is placed, air is passed through in whirling motion, and the inflammation is caused by means of a very narrow place in the tube, which causes the circuit to be closed by itself in that spot. As soon as this is done, the air-current drives on the short light-arc, primarily formed, and the result is a long light-arc, burning quietly in the centre of the tube, up to the point where the gases have become hot enough to be sufficiently conductive. An inductive resistance, placed before the light-arc, causes such a diminution of the tension during the burning of the arc that no further transit takes place in the above-mentioned narrow spot. If the arc is extinguished from any cause whatever, the relighting takes place automatically.

A great many other methods have been tried for lighting the arc, which we shall pass over here.

The whirling movement of the air is most easily produced by introducing the air tangentially into the pipe. This takes place in the recent form of the apparatus by means of eight openings, lying in a plane, bored tangentially. Several series of these are made, one over the other, and an adjustable slide permits making the light-arc more or less long, so as to work it with very different quantities of energy, and to keep up the same length of flame and approximately the same concentration of nitrogen oxides.

As the Ludwigshafen arrangements permitted working only one furnace with 300 kw., a factory was built at Kristiansand, in Norway, and started in 1907, for experimental purposes, where 1300 kw. are at disposal, and three furnaces at 500 h.p. each can be worked. Future furnaces will be made with 1000 h.p. each, and probably this can be driven to 2000 h.p. Fig. 47 gives a schematic drawing of the present furnaces. We see in the centre the insulated electrode, consisting of a strong body of copper, cooled by water. It is perforated, and in the perforation there is a movable iron rod E, forming the electrode proper, from which the light-arc starts. This rod alone is subject to wear and tear. Under the heat of the light-arc a layer of fused Fe_3O_4 is formed at its surface which evaporates slowly. In proportion as this takes place, the iron rod is moved forward. The cost of renewing the electrodes is extremely small, only a few pfennige per kilowatt and year, and a new rod is put in by simply screwing it on to the old one, in about fifteen minutes. The cooled copper body is so far removed from the iron rod that the current cannot pass over. The starting of the light-arc is brought about by rod Z, which can be moved up to the electrode. The window G, near the bottom of the furnace, makes the starting-point of the light-arc visible, so that the electrode can be moved on in the proper intervals of time. This might be done automatically by mechanical means.

The light-arc in the Kristiansand 600 h.p. furnaces is about 5 m. long, that in the 1000 h.p. furnaces, which are worked with a higher tension, 7 m. The surrounding pipe is an iron pipe which the light-arc touches only for a moment on being started, and its durability is unlimited. Its upper part is formed as a cooler, and the light-arc, by means of the regulating-slide, is driven up to this point, which can be observed by two windows, G_2 G_3, in the upper part of the furnace. It is seen there that the upper end of the light-arc continually changes its place, so that it touches a comparatively large surface of the cooler. Therefore the cooler is not subject to much wear and tear; after four months' work hardly anything of this kind could be observed; it can also be easily renewed.

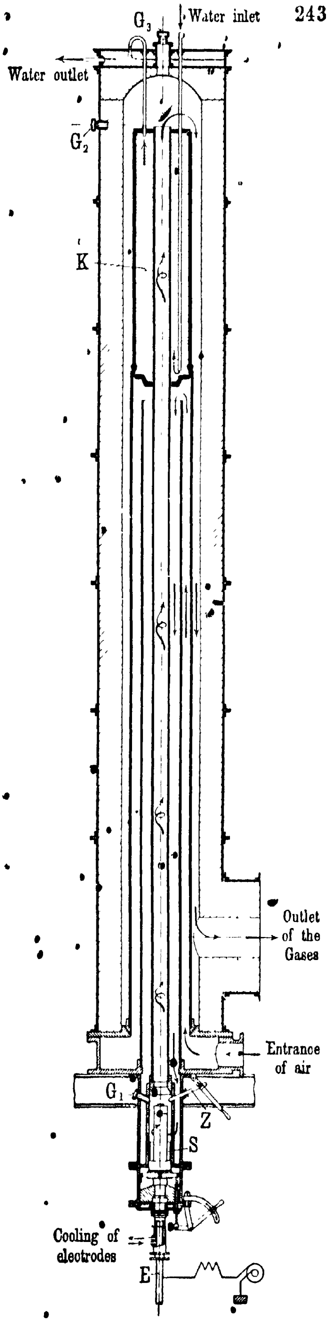

FIG. 47.

After passing through the cooler, the gases descend in a brick-lined channel surrounding the inner part of the furnace; they go to a common flue and from this into the steam-boiler which serves as further cooler, and the steam from which serves for concentrating the liquors produced in the process. On descending in the furnace they give up part of their heat to the pipe by which the fresh air is supplied to the furnace. The drawing shows how this air first rises upwards and receives heat from the outgoing hot gases; it turns round within the cooler, passing the innermost pipe which encloses the light-arc, and is thus further heated, so that it arrives sufficiently hot through the afore-mentioned tangential borings in the flame-pipe itself.

The vertical arrangement of the flame is not essential; it may also burn horizontally. The air may also be sent through from the top downwards; and if the pipe is short enough and open at the opposite end, an enormously hot blast-flame is formed of strongly oxidising properties. Such an arrangement can be used for oxidising or reducing fusions, according to the nature of the gas employed. In this case the charge and the fusion vessel itself serve as second electrode.

Several other modifications are described in Schönherr's paper. He states that the duty factor of their light-arcs is 0·92 to 0·96; the long time of contact, which has been found fault with by some critics, just favours the utilisation of the energy expended. Still, of the total energy spent upon the light-arc, only about 3 per cent. are actually expended in the *formation* of NO; but apart from this a large quantity of highly heated air is obtained, of which certainly only a small proportion is utilised for other purposes. The preheating of the air in iron tubes cannot very well be driven beyond 500°. Of the total heat brought in by the light-arc, 40 per cent. is recovered in the shape of hot water, 17 per cent. is lost by radiation, 30 per cent. is utilised in the steam-boiler, and another 10 per cent. must be taken out of the gases by cooling with water after leaving the boiler, so that only 3 per cent. are utilised for the formation of nitric oxide. The heat going out in the shape of hot water and steam might be utilised for other purposes; the steam is used for boiling down the liquor, so that the factory requires no other sources of heat except the electric energy.

We have seen that, after the heating of the air, there must be a sudden cooling. This need not be carried further than down to 1200° to 1500°; the velocity of decomposition of NO is then small enough to allow of taking out the remaining heat without any loss of nitric oxide. The gases in fact leave the flame-pipe at 1200°, and on entering the common gas flue they are at 850°. When the temperature has gone down below 600°, the colourless NO combines with more O, from the air present in excess, and yields brown-red gaseous nitric peroxide, NO_2. This oxidation is only perfect below 140° and takes some time. A gas mixture containing 2 per cent. NO, cooled down to 20°, requires twelve seconds for the oxidation of 50 per cent., or one hundred seconds for the oxidation of 90 per cent. of the NO present. The utilisation of this nitric peroxide is not quite a simple matter. Alkaline liquids, like solutions of sodium carbonate or milk of lime, absorb it with formation of equal parts of nitrate and nitrite, and these mixtures can be used directly for manurial purposes. The former statements as to the alleged noxious effect of nitrites on plants have been entirely refuted by the investigations of Lepel, Schlösing, and Wagner, which have proved beyond any doubt the equivalence of nitrous with nitric nitrogen for the plants.

The application of soda solution is out of the question on account of the cost, and that of milk of lime is connected with difficulties, as ordinary flushing towers are quickly stopped up. These difficulties have now been overcome, and the *nitrite of lime* obtained contains 18 per cent. nitrogen, against only 15 per cent. in Chilian nitrate of soda, and 13 per cent. in the Norge saltpetre, brought into the trade from Notodden. For that matter, the nitrite might be easily converted into nitrate, if required.

At Notodden (Birkeland and Eyde's process) most of the absorption takes place by means of water; thus free nitric and nitrous acid are formed. The latter decomposes into HNO_3 and NO, which goes out with the air and is again oxidised to NO_2, and must be treated as before. The last portions of NO are in that factory absorbed in soda solution and yield pure sodium nitrite, for which there is a sale in the manufacture of azo-dyes. If it is washed, the whole of the NO produced may be converted into sodium nitrite by the Badische Ger. P. 188188, which is carried out at Kristiansand. But the market for this product is limited.

The oxidation of the NO and the absorption of the higher nitrogen oxides requires large spaces, and special arrangements are made for this purpose, such as the interposing of oxidising spaces in which the gases remain for some time (*vide infrà*). The absorption by sulphuric acid, with formation of nitric and nitroso-sulphuric acid, is easy, but the utilisation of this product is not quite easy outside of sulphuric acid works. Other methods proposed are also not fit for a very large production, and there is still room for improvements in that field.

In conclusion, Schonherr mentions the various projects for further establishments, to be founded in various parts of Norway by the Badische Anilin- und Sodafabrik, associated for that purpose with the Elberfelder Farbenfabrik, the A. G. for Anilinfabrikation, Berlin, and the Norsk Hydro-electrisk Kvaelstofkompagni. Upwards of 400,000 h.p. in the shape of water-power has been secured for that purpose. In Germany as well the Badische will carry out their process by means of 50,000 electric h.p., obtained from the water of the Alz, the outlet of the Chiemsee.[1]

Bernthsen (*loc. cit.*, p. 1174) points out that the concentration of NO in the Badische (*i.e.* Schonherr's) apparatus is = 2 per cent., *i.e.*, from one and a half to two times as great as in the Birkeland-Eyde apparatus.

The patents of the Badische Anilin- und Sodafabrik are as follows :—

A. For producing light-arcs.

B. Ps. 5688 and 26602 of 1904; 14955 of 1905; 9279 of 1906; 20406 of 1908; 10465 and 20129 of 1909. Ger. Ps. 168601; 201279; 204997; 212051; 212501; 212868; 219494; 223586; 227012; 229292; Ger. P. appl. B54700. Fr. Ps. 357358; 410710; 418892; 396375. Amer. Ps. (of Schönherr and Hessberger) 991174; 1003279.

B. For absorption of nitrogen oxides.

B. Ps. 10465, 10867, 11274, and 20502 of 1909. Ger. Ps. 188188; 210167; 212868; 220539; 229780; 223026; 223556;

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[1] In June 1911 the newspapers report that, owing to difficulties which have arisen about the water-power of the Alz, the Badische had given up their project of erecting a factory there.

232926; 233586; 233729; 233967; 233982; 237562; 238369. Fr. Ps. 363643; 411574; 412788; 398738. Amer. P. 991356.

Apart from their share in the Notodden works (Birkeland and Eyde's process), the Badische are making installations at Vernork, near Saaheim in Telemarken, where the Rjukan falls yield 195,500 h.p., and an annual production of 80,000 tons nitre, of a value of 13,000,000 marks is expected. The same concern is building a factory in Norway, utilising the falls of the Tya River, of about 70,000 h.p.

Utilisation of the Nitrous Vapours obtained by the Oxidation of Atmospheric Nitrogen.

The conversion of the very dilute nitrous gases, obtained by the above-described processes, into marketable products is not quite an easy matter. Several final products can be obtained therefrom, such as free nitric acid, or nitrates, or nitrites; and even liquid nitrogen peroxide has been made from them. The demand for the latter will hardly ever be considerable; nor is there any chance of greatly increasing that of sodium nitrite, of which a few thousand tons per annum are consumed for the manufacture of azo-colours. The consumption of nitric acid is far more considerable, but the expense of the glass carboys or other means of transporting that acid prevents its manufacture on a very large scale, more particularly as nearly all of that acid is consumed at places very far distant from those where the abundance of water-power admits of the manufacture of nitrogen oxides from air. On the other hand, the consumption of nitrates for agricultural purposes is practically unlimited, and as these are easily and cheaply carried to any distance by land or by water, the principal task will always be that of ultimately fixing the atmospheric nitrogen in this shape, although in the first instance the production of nitric acid as an intermediate product must take place.

Among the nitrates, that of *calcium* takes a prominent part in the industry here described, as, on the one hand, it is much cheaper to make than sodium nitrate, and, on the other hand, its value for agricultural purposes is quite as great, and that for chemical manufactures, *e.g.* that of nitric acid and indirectly that of explosives, nearly as great as the value of sodium nitrate. The general principle to be followed here has been several times touched upon in the preceding descriptions. In the first instance the atmospheric nitrogen is always converted into nitric oxide, NO, and this, as well known, very easily passes over into peroxide, NO_2 or N_2O_4. If the gases are brought into contact with water in towers or similar apparatus, the nitric peroxide yields equal molecules of nitric and nitrous acid; the latter quickly decomposes into nitric acid and NO, and this is carried back into the process, so that ultimately the whole of the nitrogen oxides is converted into nitric acid, which is always dilute, say 40 per cent. HNO_3. This dilute nitric acid is either concentrated for sale as strong acid, or, on account of the aforesaid difficulties, it is more frequently converted into calcium nitrate by means of limestone. That nitrate can also be obtained in the dry way by passing the gases over quicklime; or, according to the patents of the Badische Co., in the wet way by direct absorption of the gases in milk of lime. The calcium nitrate thus obtained now forms an important article of trade, usually under the name of *Norge saltpetre* (Norwegian nitre), *see* p. 238.

We have had frequent occasion to refer to the treatment of the lower nitrogen oxides for commercial products in the above given descriptions of various processes for oxidising atmospheric nitrogen, and we shall now enumerate the more recent processes worked out in that line, partially not yet mentioned before. In that respect, *cf.* also the processes employed for the treatment of the lower nitrogen oxides in the manufacture of nitric acid by the ordinary methods, *suprà*, pp. 182 *et seq.*

The Badische Anilin- und Sodafabrik has taken out a number of patents for dealing with the dilute nitrous gases in various ways.

B. P. 10867 of 1909 and Ger. P. 210167 of the Badische Co. describes the manufacture of commercially pure nitrates by adding limited quantities of aqueous vapour to the gaseous mixtures produced by the electric arc flame from air, by passing these gases over the solid oxides, hydroxides or carbonates of the alkaline earth metals, while maintaining these at such a temperature that all the water set free remains in the state of vapour. This produces practically pure nitrate. If magnesia is employed as the absorbing agent, the addition of steam or water to the gases can be dispensed with, as magnesium nitrate is stable at a temperature at which magnesium nitrite splits up.

The same firm (B. P. 10465 of 1909) absorbs the nitrous acid from the gaseous mixture by introducing into it milk of lime, or other suitable bases, in the state of fine division, *e.g.* by means of a spray.

Their Ger. P. 229780 prescribes the application of a spray-producer, worked by a compressed gas issuing from a narrow orifice, which is in the centre of the tube conveying the liquid to be converted into a spray, for removing nitrous acid from its solutions.

Their Ger. P. 231805 describes the preparation of nitrogen peroxide, free from nitric acid, by drying washed NO by means of concentrated sulphuric acid, and combining it with dry oxygen or air.

The same firm (Fr. P. 412788 and Ger. P. appl. B52866) absorbs nitrous gases by means of finely divided bases, suspended in water, and, in order to observe the reaction, glass windows are placed in suitable places of the apparatus; by means of a door in the side the atomiser can be cleared of obstructions without stopping the working of the apparatus.

According to Ger. P. 232926, that firm absorbs nitrogen oxides, whether pure or mixed with air, etc., by the oxide, hydroxide, or carbonate of magnesium, at a temperature at which no nitrite, but only nitrate of magnesium is formed.

Their Ger. P. 233729 precipitates the fogs occurring in nitrous gases by passing them between a sparking and a non-sparking electrode, the latter being formed by the walls of a cylindrical vessel, in which the sparks are produced by pointed electrodes.

Their Ger. P. 233967 describes the supply of basic agents for the absorption of nitrous gases without the application of towers, in the shape of drops, which avoids the trouble caused by the formation of sludge. Ger. P. 233982 protects for that purpose the application of spray-producers, into which the liquid is introduced tangentially at the basis, that basis being formed of glass or other transparent material. In this way a whirling motion is produced, visible through the glass as a point or disc; any irregularity of work is recognised by the enlargement or diminution of that dark disc. Their Ger. Ps.

238367 and 238368 describe processes for producing continuous long light-arcs.

Their Ger. P. 238369, Fr. P. 398738, converts alkaline-earth nitrites into nitrates by treating them at 300° with the higher oxides of nitrogen in the presence of air; NO is also produced, which acts as a carrier of oxygen to a further quantity of nitrite.

The same firm (Amer. P. 991356) makes nitrate and nitrite of sodium by passing nitrous gases through a series of towers, passing a 20 per cent. sodium carbonate solution in the opposite direction through part of the series, separating the nitrite from the solution that has traversed this part of the series, and separating the nitrate from the residual solution, after passing it through the remainder of the series.

Among all metals, only iron, aluminium, and chromium produce nitrates, which on heating with water give off nitric acid without any products of decomposition of this acid. When heated at ordinary pressures, nitric acid begins to distil over at 115-125°; and by gradually heating up to 145°, so much of it distils off that basic nitrates of the desired composition remain. When heating in a vacuum, *e.g.* of 20 mm., the distillation of nitric acid begins at 55-60°, and is finished at 75-80°.

The same firm's Ger. P. 243892 shows how concentrated vapours of N_2O_3 can be obtained by treating the liquors, produced according to the preceding patent, by the products of absorbing the dilute nitrous gases in caustic alkali or alkaline earths in the well-known manner. Thereby pure alkaline or earthy-alkaline nitrates are formed, together with the hydroxides of iron, aluminium, or chromium, which are used over again, as above described.

Ger. P. 242288 of the Badische describes the preparation of pure nitrogen peroxide from gases containing but little of it, by compressing them to 6 atm., taking the heat of compression away and allowing the gases to expand adiabatically, whereby such cooling is effected that the higher nitrogen oxides separate in solid shape. For this, temperatures of about 80° are sufficient. The energy produced by the expansion may be utilised for doing work; also the cold produced by the expansion for cooling the compressed gases, or by dehydrating the original gaseous mixture.

The Farbenfaberken vorm. Bayer (Ger. P. 228426; Fr. P.

423760) separate nitrogen oxides from gaseous mixtures by absorbing them in wood-charcoal, and recovers them from this in a concentrated form by treatment with dry high-pressure steam, hot air, or an indifferent gas.

Schlarb (Fr. P. 422751; Amer. P. appl. 2427 of 1911; Ger. P. 273839) absorbs nitrous gases of any degree of concentration and composition by mixtures of water with oxides of iron, aluminium, or chromium, if necessary with addition of alkali, alkaline earths, or magnesia. From these liquors nitric acid is obtained by heating, preferably in a vacuum or under diminished pressure. The basic constituents remain behind, and can be used over again after removing the nitrates formed. It is stated that by this means nitric acid of 50 to 80 per cent. can be obtained.

The Soc. Le Nitrogène (Fr. P. 421022) introduces into the gases containing nitrogen oxides a small quantity of a solvent, which freezes below 50°, boils above 50°, and is capable of dissolving N_2O_4 without attacking it, like carbon tetrachloride, chloroform, or pentachlorethane, or mixtures of these, brought into the refrigerating portion of an apparatus in which nitrogen oxides are prepared by igneous synthesis from N and O. These solvents maintain the continued efficacy of refrigeration, as they dissolve the N_2O_4, and prevent this from forming a non-conducting crust on the outside of the cooling apparatus. The addition of powdered animal charcoal to the gases before cooling renders the condensation and solution of N_2O_4 possible at a higher temperature than when such addition is not made. The Fr. P. 421313 of the same firm prescribes depriving the gases before refrigeration from moisture and CO_2, before compressing and washing out the apparatus after refrigeration with a solvent like those mentioned in the last patent. Their Fr. P. 424598 states that concentrated nitric acid can be obtained by treating a molecular mixture of N_2O_4 and H_2O with oxygen under pressure, or by charcoal soaked with a peroxide.

Baron Vietinghoff-Scheel (Ger. P. 225706) states that the reaction between NO_2, O, and H_2O is essentially promoted by high pressure, and that in this way more highly concentrated nitric acid can be obtained than by flushing towers, etc.

Sir W. Ramsay (B. P. 26981 of 1907), to increase the efficiency of absorption of the nitrogen oxides, liquefies the mixed gases, after cooling them by the gaseous products of the liquefying apparatus; by fractional liquefaction the oxides of nitrogen can be separated; or else the liquefied product is subjected to evaporation and rectification, to concentrate the oxides of nitrogen.

The Elektrochemische Werke (B. P. 9233 of 1908; Ger. P. 199561) pass the mixture of air and NO_2 through a drum rotating at high speed, cooling the gases either before entering the drum or in the drum itself. The gases ought to come entirely into contact with the walls of the drum. The mist of water and condensed N_2O_4 is forced by centrifugal action against the wall of the drum, from which the liquid is continuously drawn off. A little steam may be mixed with the gases before entering the drum.

Another process of the Elektrochemische Werke (Ger. P. 212423; Fr. P. 411693) consists in taking the nitrogen oxides out by weakly basic oxides, such as those of Zn, Cu, Mg, or Pb, or the rare earths, and expelling it from these compounds in the shape of concentrated nitric acid by well known methods. If the powdered oxides are agitated during the passage of the gases, the absorption goes on very quickly, completely, and up to the formation of neutral salts. These are gradually heated in iron retorts, where the absorbed nitrogen oxides are given out as NO_2. This may be condensed and sold as liquid N_2O_4, or oxidised into HNO_3 in appropriate water-fed towers.

The General Electric Co. (Amer. P. 921975) pass a mixture of nitric oxide and air over a weak basic oxide, and decompose the product by heating under reduced pressure; the liberated gas is absorbed by water and yields commercial nitric acid.

Bideau (Fr. P. 396299) prepares nitrosulphuric acid by conducting nitrous vapours, by means of a fan, into cast-iron vessels containing sulphuric acid. For the preparation of dilute nitric acid the apparatus is constructed of stoneware.

The Allgemeine Elektrizitäts-Ges. (B. P. 8426 of 1908) absorb the oxides of nitrogen by weak bases, such as oxides of Zn, Cu, or Pb; the mixture of nitrate and nitrite thus obtained is afterwards decomposed by heating, if desired under reduced pressure, with evolution of pure nitrogen peroxide.

The Norsk Hydro-Elektrisk Kvaelstof A.S. (Ger. P. 206949; Birkeland's B. P. 25632 of 1907) absorb the nitrous fumes, obtained by the electrical oxidation of atmospheric nitrogen, by calcium cyanamide, thus obtaining a mixture of ammonium and calcium nitrate, valuable as a fertiliser. The nitrous fumes are readily and completely absorbed in this way.

Ostwald (Ger. P. 207154) prescribes nickel steel for the construction of all parts of apparatus coming into contact with hot nitrogen oxides, but care must be taken to prevent any condensation of these gases.

Bergius (Ger. P. appl. B53617) mixes the gases produced in the light-arc, containing about 2 per cent. NO_2, with O_2 and H_2O, and compresses the mixture to about 25 atm., whereupon it is passed through a heated reaction-space in which the formation of HNO_3 takes place, the pressure preventing the decomposition otherwise produced by the heat.

The Swedish Nitric Syndicate (Austr. P. 43740) effects the concentration of electrically produced nitric acid in two stages, the first by contact with hot air, the second by distillation of the partially concentrated nitric acid with sulphuric acid, utilising the heat of the same gaseous current.

Brunet, Badin, and the Compagnie des Produits chimiques d'Alais et de la Camargue (Ger. P. 237796) describe horn-shaped electrodes for the production of nitrogen oxides by the electric arc.

Moscicki (Ger. P. 236882) and Ellis (Amer. P. 1007683) also describe arrangements for this purpose.

Sparrl (Amer. P. 1008383) converts nitrogen protoxide in solutions into NO by passing it through a diaphragm apparatus with high anodic and low cathodic current-densities

R. Frank and the Siemens and Halske Co. (Ger. P. 246615) utilise the dilute nitrogen oxides, produced by the electric arc, which cannot be easily and cheaply transformed into dry salts, by bringing them with complete exclusion of moisture into contact with the halogen-hydrogen acids, or the vapours of these. Further patents in this line: Farbwerke Hochst (Ger. P. 244362); Koch (Fr. P. 435733).

Nitric Acid from Ammonia.

Theoretical investigations on the oxidation of ammonia or ammonium salts to nitric acid which, of course, has been known to occur for a long time, and which has been especially studied by Schonbein during the years 1845 to 1867, have been recently made by the following authors.

Kempf (*Berl. Ber.*, 1905, xxxviii. p. 3966).

Traube and Biltz (*ibid.*, 1906, xxxix. p. 166) proved the anodic oxidation of NH_3 in solutions of fixed alkalis or carbonates by means of copper salts. At ordinary temperatures nitrites are formed almost quantitatively, and only when the solution contains much nitrite, this is partly oxidised to nitrate.

Müller and Spitzer (*Z. Electrochem.*, xi. p. 917) found that the anodic oxidation of NH_3 in alkaline solutions goes on up to nitrate only when anodes of platinum or cobalt are used; otherwise only nitrites and free nitrogen are formed. The yield is increased by the addition of salts of copper, cobalt, or nickel, or by the use of anodes consisting of metallic oxides.

Besson and Rosset (*Comptes rend.*, cxlii. p. 633) examined the action of N_2O_4 upon NH_3.

Böcker and Schmidt (*Berl. Ber.*, 1906, p. 1366) studied the oxidation of NH_3 by platinum asbestos, according to Ostwald's process (see below), and came to the conclusion that this process cannot pay.

Brochet and Boiteau (*Z. angew. Chem.*, 1909, p. 1234) found ammonium nitrate as main product of the electrolytic treatment of NH_3 by means of graphic electrodes. When employing platinum or iron electrodes, the phenomena were complicated. The oxidation of NH_3 to HNO_3 requires great quantities of current.

Bourgerel (*Monit. Scient.*, 1911, pp. 561-575; *Chem. Zeit. Rep.*, 1911, p. 621) discusses the preparation of aluminium nitride for the fixation of atmospheric nitrogen. He calculates the cost price of chemically active nitrogen at 1·77 frs. per kilogram, that is more than that contained in Chili sodium nitrate, which is only 1·50 frs. per kilogram (taking the price of Chili nitrate = 23 frs. per 100 kg.). The cost price of active nitrogen in the shape of electrolytically produced nitric acid he states = 0·91 frs. per kilogram.

Reinders and Cats (*Chem. Centr.*, 1912, i. p. 708) found that in a mixture of NH_3 and air, when passing it over catalysers, up to 80-90 per cent. could be oxidised into HNO_3 and N_2O_3. The best temperature for this was 600° in the case of platinum, and 650-700° in that of ferric oxide.

The following patents refer to the technical production of nitric acid, nitrates (or nitrites), from ammonia :—

Stuart-Bailey (B. P. 19189 of 1905) manufactures sodium nitrate by oxidising NH_3 to ammonium nitrate or nitric acid, and treating the product with electrolytically made caustic soda.

Nordyke and the Marmon Co. (Ger. P. 189472; B. P. 1204 of 1906) describe an apparatus for producing nitrogen oxides from NH_3 and air by electrical heating in a spiral platinum tube.

Marston (B. P. 19074 of 1900) passes such mixtures over red-hot copper, iron, or other oxidisable metals.

Kéler and the Farbenfabriken Bayer in Elberfeld (B. P. 18594 of 1903; Amer. P. 763491; Ger. P. 168272) pass a mixture of air with 4 or 5 vol. per cent. of NH_3 at temperatures of 600° to 750° over catalysers, consisting of the oxides of heavy metals, especially ferric oxide, and absorb the product in alkaline solutions. In this way almost exclusively nitrites are formed.

The Chemische Fabrik Griesheim-Elektron (B. P. 13954 of 1907; Fr. P. 380884; Amer. P. 971149, etc.; Ger. P. appl. C17336) employs for the production of nitric acid from ammonia a catalyser, consisting of quartz or newly-glazed porcelain, on which platinum is precipitated as a very thin film and heated up to sintering together with the underlying body. This prevents a loosening of the platinum surface, such as happens in ordinary cases during the process and which causes a decrease in the efficiency of the contact surface. This process is in operation at Griesheim.

Collett and Eckardt (B. P. 10815 of 1909) prepare nitrate of lime from (electrically produced calcium) cyanamide in the following manner. The nitrogen of calcium cyanamide is transformed into ammonia by saponification, heating it with aqueous nitrate of lime. This ammonia is oxidised and transformed into nitric acid or nitrogen oxides. The novelty of the patent consists in the arrangement of the various stages, as all the steps are known.

Kaiser (B. P. 20325 of 1909; Amer. P. 987375; Fr. P. 419782) preheats the air to 300° to 400° before mixing it with the ammonia, prior to passing it over a heated contact substance, such as platinum wire gauze (Ger. P. appl. K42005).

The same inventor (Ger. P. appl. K40923) carries the air, before mixing it with ammonia, over a heated contact substance (platinum, etc.), or subjects it to electric discharges.

Very much work in this direction has been done by the celebrated Professor Ostwald, whose patents we shall now enumerate. In *Berg- u. Hüttenm. Rundschau*, 1906, p. 71, he states as a principal condition for his processes a definite velocity of the reacting gases and the employment of cathodes of platinum foils coated with spongy platinum.

W. Ostwald (B. P. 698 of 1902) passes ammonia, with more or less than its volume of atmospheric air, at a red-heat over smooth platinum, coated with a layer of spongy or black platinum. The smooth platinum causes the ammonia to be burnt into nitric acid, with practically no formation of free nitrogen. The finely divided platinum accelerates both reactions, the second one more than the first. By moderate use of the finely divided platinum with the smooth platinum, the operation can be so performed that the reaction takes place rapidly, but without any great formation of free nitrogen. The same effect is produced by iridium, rhodium, palladium, the peroxides of lead and manganese, the oxides of silver, copper, iron, chromium, nickel, and cobalt. Later on Ostwald (Addition, dated 9th April 1902, to Fr. P. 317544; *cf.* B. Ps. 698 and 8300 of 1902) gives the following additional prescriptions. The air must be in considerable excess, the temperature of the reaction must exceed 300° C.; the passage of the gaseous mixture must be as rapid as possible, and the gases are previously heated by the hot gases coming away from the contact-mass. The apparatus consists of an open tube, charged at one end with the contact-material (platinum coated with platinum sponge), fixed air-tight in a cylinder with its open end projecting. The cylinder has an aperture close to the exit end for admission of the gases, which thus pass along the sides of the tube before entering through the end containing the contact-material. The gases, strongly heated by the reaction, heat the tube on their passage onwards, such heat being in part taken up by the entering gases.

Ostwald (Amer. P. 858904) produces nitric acid from a mixture of NH_3 and air (or other source of oxygen) by means of any contact substances, among which a combination of platinum foil with platinum sponge has the best action.

Gaseous mixtures containing very little NH_3 can be worked up with advantage by gently heating, but there should be at least as much NH_3 in proportion to oxygen as corresponds to the formula: $2NH_3+7O=2NO_2+3H_2O$. The velocity of the gaseous current must not be too small, lest free N be formed. The contact substance should be kept at a temperature above 300°; this is produced in the first instance by heating with a flame or electrically, and later on by regulating the gaseous current. His B. P. 7909 of 1908 (Fr. P. 389059) prescribes arranging sheets of catalytic material parallel to one another, so as to fill the entire cross section of the chamber in which the reaction takes place. The plates and the spaces between them are inclined to the axis of the chamber and in the direction of the entering gases. The plates are fixed in such manner that they make contact at very few points and thus minimise their resistance to the passage of the gases.

Ad. Frank and Nic. Caro (Ger. P. 224329) prepare nitric acid from NH_3 by the catalytic action of thorium oxide, or mixtures of this with the oxides of the other rare metals. By the intermediate formation of thorium nitrate a strong swelling of the mass is produced which leaves the contact mass in a porous, very active state, while the thorium sulphate, formed in the use of thorium oxide for the catalytic production of sulphuric acid (B. P. 1385 of 1901), on heating yields a very dense, non-porous oxide.

Wendriner employs for the same purpose uranium or its salts as catalysers (*Chem. Ind.*, 1911, p. 456).

Montbaron and Ducommun-Muller (Fr. P. 400895) ferment ammoniacal liquor, obtained from peat, with addition of nitric acid, lime, and impure salt; nitrification is brought about and the product is crystallised for use as a manure. One ton of the product requires 320 kg. ammoniacal liquor, 300 lime, 300 salt, and 80 nitric acid.

Stuart-Bailey (B. P. 19189 of 1905), starting from carbonaceous matter containing nitrogen, subjects this to destructive distillation, utilising the NH_3 in the usual manner, and the combustible gases for the production of electricity which he utilises for decomposing common salt. The NH_3 is passed with air or oxygen over heated platinum, to obtain nitric acid, and ultimately sodium and ammonium nitrate.

Storage and Carriage of Nitric Acid.

Strong nitric acid can be kept and treated in cast-iron or wrought-iron or leaden vessels, but, of course, any dilution caused by the moisture of air or otherwise will cause a violent action. Aluminium resists nitric acid even in a somewhat more dilute state.

At the Griesheim Chemical Works a covered lead spout below the outlet of the nitric-acid store tank for the highly concentrated nitric acid takes this acid to the carboys. This spout is connected with an aspirator for the vapours, and turns round a bolt, fixed below its central port, so that the carboys can be easily and safely placed below.

Transportation of Nitric Acid.—Nitric acid is usually sent out in glass carboys or earthenware jars. Strong acid, when kept in tightly closed vessels, may give off a dangerous amount of vapours, especially in the sunshine or under similar conditions. Guttmann recommends covering the carboys loosely with earthenware or glass cups fitting over the necks, also making the straw in which the carboys are packed incombustible by dipping it in a solution of zinc chloride or nitre-cake [which will very quickly corrode it; neutral sodium sulphate is decidedly preferable!], and to limewash the top of the carboys exposed to sunlight; also to store the carboys in an excavated chamber, where a breakage will not cause much damage, as the place can be swamped with water. Sometimes fires are caused by nitric acid from a broken carboy inflaming the straw; in which case the poisonous vapours are exceedingly dangerous to inhale (*cf.* Chapter VI.).

The "Mauserwerk" at Cologne-Ehrenfeld manufactures for nitric-acid carboys baskets, made of sheet-iron, with a lining of asbestos felt. The latter affords a soft surface for the glass to touch; the absence of any combustible (like straw) greatly diminishes the danger from fire, incident upon the breaking of the carboy.

Another arrangement of this kind, patented by Adamson (Amer. P. 846541) will be described in Chapter V.

The official rules for conveying nitric acid on the English railways, published in 1911 (*Chem. Trade J.*, xlviii. p. 568), state that nitric acid or aquafortis may be packed (*a*) in stoneware jars, protected by wickerwork; (*b*) in bottles, packed in cases or boxes; the interstices between the bottles must be filled with kieselguhr, or with other material on which the acid has no chemical action, *not* with sawdust, straw, or other like substance. Sulphuric acid, inflammable liquids, or other chemicals which by contact with nitric acid might cause fire or explosion must not be packed in the same case or box; (*c*) nitric acid or aquafortis not exceeding 1·420 sp. gr. may be packed in glass carboys not exceeding 12 gall. in capacity.

For conveying larger quantities of nitric acid, in some places specially strong stoneware jars are employed, with inside flanges for the purpose of strengthening the sides; the bottom is arched upwards for the same purpose, as shown in Fig. 48.

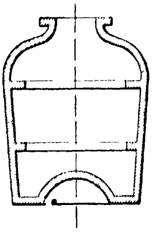


FIG. 48.

Mixtures of sulphuric and nitric acid, containing up to 80 per cent. of the latter, can be carried in iron vessels.

Sometimes nitric acid, in order to facilitate its transportation, is absorbed in *kieselguhr* (infusorial earth), a plan first proposed by Vorster and Gruneberg (Ger. P. 24748) for the carriage of sulphuric acid, especially by sea.

Hale and Scott (B. Ps. 24379 and 25386 of 1910) recover nitric acid from its mixture with kieselguhr by distillation, preferably in a heated retort under reduced pressure, the mass being mechanically stirred so as to keep it at a uniform temperature.

Pumping of Nitric Acid.—For this purpose Paul Kestner, of Lille, has constructed special "pulsometers" entirely of stoneware, one form of which is shown in Fig. 49—exhibiting the cylinder A, the float B, the air-valve C, and the delivery-pipe D. All flanges are made tight by thin sheet asbestos, the faces being ground and polished. The working of this "pulsometer" is exactly like that of the cast-iron pulsometer described in Chapter VI.

Another automatic and continuous pulsometer has been constructed by Plath, and is sold by the Vereinigte Thonwaarenwerke, Charlottenburg (Fig. 50). It also consists entirely of stoneware, including the valves. The acid enters through valve *a*, the hollow ball of which is weighted so that

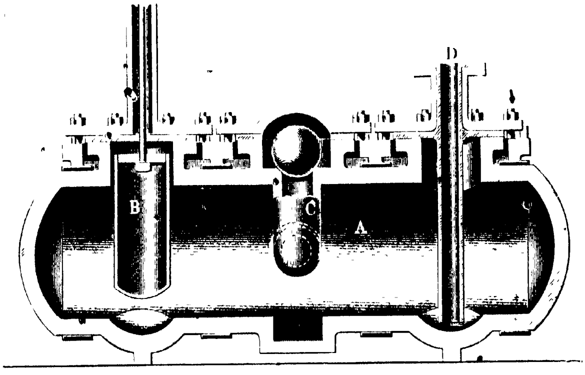
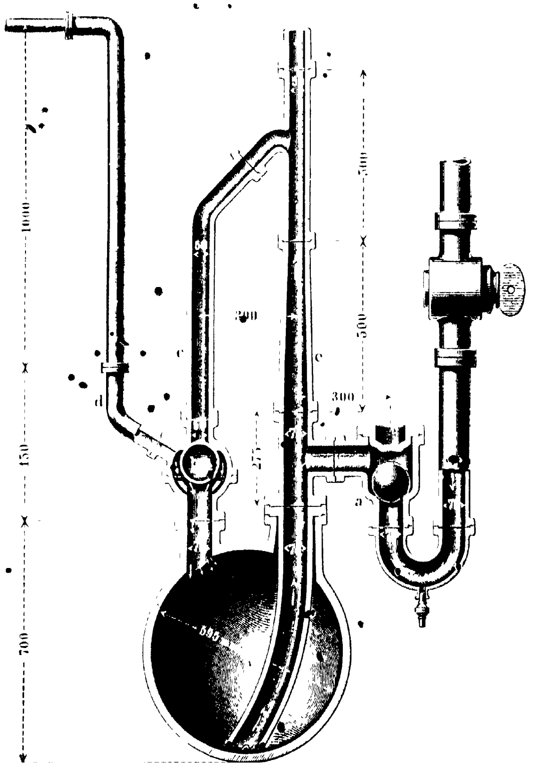


FIG. 49.



it just sinks in the liquid, and is therefore easily raised by the inflowing liquid. When the vessel is full, the acid gets up to the other valve, the ball of which, *b*, is so light that it even floats upon water. It is, of course, raised by the acid and shuts off the upper air-way *c*. The compressed air now enters through *d* and forces the acid up into the rising-main *e*, and thus into the upper store-tank. As soon as the vessel is empty, the ball *b* descends, being aided by the short column of liquid in *c*. The compressed air cannot now enter the vessel, and, as there is now no counter pressure, the ball *a* is again raised and the acid flows in from the lower tank, the air escaping through *c*. This action continues so long as there is acid in the lower store-tank and compressed air in *d*. Balls *a* and *b* are accurately ground as usual for pumps, etc. A new model made by the same firm prevents any escape of compressed air during the charging.

Schartler (*Z. angew. Chem.*, 1901, p. 729) describes apparatus constructed by O. Guttmann from stoneware for the purpose of raising acids, viz., first an injector for working with steam or compressed air, and, secondly, a constantly acting acid-egg.

Analysis of Nitric Acid.

Nitric acid is frequently merely tested by the hydrometer, but this is quite illusory, owing to the influence of the nitrogen peroxide (p. 137). When tested by titration it should be noticed that methyl-orange is destroyed by nitrous acid; but this can be overcome by adding the indicator only towards the end of the titration (*cf.* Chapter III., where the indicators are more specially treated). When titrating with caustic soda, this indicates all acids: HNO_3, N_2O_4 (which reacts $= HNO_3 + HNO_2$), H_2SO_4, etc. At least a permanganate titration should be made as well, in order to estimate N_2O_4.

The *impurities contained in commercial nitric acid* are as follows:—*chlorine, sulphuric acid, fixed residue, iron*: all found and estimated by well-known methods. *Nitrous acid or nitrogen tetroxide* is best estimated by means of potassium permanganate, running the acid from a burette into the warm diluted solution of permanganate, as will be described in the next chapter. (The influence of NO_2H on the specific gravity of nitric acid has been noticed, *suprà*, p. 137.) *Iodine* is recognised by boiling 1 c.c. in order to remove the lower nitrogen oxides and to oxidise all iodine into iodic acid, diluting with 5 c.c. previously boiled water, and adding a few drops of a solution of potassium iodide and starch, made with water free from air. A blue colour shows the presence of iodine in the original acid, according to the reaction

$$HIO_3 + 5KI + 2H_2O = 5KOH + 6I.$$

This test, according to Beckurts (*Fischer's Jahresber.*, 1886, p. 305), is much more delicate than the ordinary one of reducing the iodate by zinc and extracting the iodine set free by carbon bisulphide; but Beckurts's test would, of course, lead to serious errors unless a check test was made with the iodide of potassium employed, which might itself contain some iodate.

Protection against Accidents caused by Fumes of Nitric and Nitrous Acid.

In Chapter VI. we shall treat of this subject in connection with Gay-Lussac and Glover towers. I will here only allude to the official rules published by the "Berufsgenossenschaft fur chemische Industrie," *Fischer's Jahresber.*, 1899, p. 411, the report by Duisberg, *Z. angew. Chem.*, 1897, p. 492, and the rules published in the *Deutsche Reichsanzeiger* of 31st March 1899 and 19th June 1903.

Statistics.

Statistics concerning nitric acid are very difficult to obtain. In the United States, in 1902, 27,890 tons nitric acid of various strengths were made; in 1905, 108,380 short tons; in 1909, 69,000 tons as chief product, 9500 tons as by-product, and 55,500 tons for use in the factories themselves; besides 28,600 tons of "mixed acids" (U.S. Census Bulletin).

The United Kingdom exported in 1908, 5141 tons nitric acid; in 1909, 5385 tons; in 1910, 3716 tons.

CHAPTER I

HISTORICAL AND GENERAL NOTES ON THE MANUFACTURE OF SULPHURIC ACID

History of the Manufacture of Sulphuric Acid.

ACCORDING to Rodwell (*Birth of Chemistry*) it is very probable that sulphuric acid was already known to the ancients; but usually its first, although indistinct, mention is ascribed to the Arab Geber, who speaks of the "spirit" which can be expelled from alum and which possesses solvent powers. Geber is, however, a mythical personage, and many of his alleged numerous discoveries have wrongfully crept into the Latin "translations" of his pretended writings, as proved by Berthelot and Steinschneider (*cf.* Lippmann, *Z. angew. Chem*, 1901, p. 646), who show that sulphuric acid was unknown to the Arabian writers about 975 A.D. Others give the honour of its discovery to the Persian alchemist Abu-Bekr-Alrhases, who is said to have died in 940. Vincentius de Beauvais (about 1250) alludes to it; and Albertus Magnus (1193-1280) speaks of a *spiritus vitrioli Romani*, which can only have been sulphuric acid; his "sulphur philosophorum" is the same thing.

With all distinctness Basilius Valentinus, who has probably lived in the second half of the fifteenth century, in his *Revelation of the Hidden Manipulations*, describes its preparation for calcined copperas and silica, and, in his *Triumphal Car of Antimony*, also its preparation by burning sulphur with saltpetre (Kopp, *Geschichte der Chemie*, iii. p. 303); but he took the two to be different substances.

Gerhard Dornæus (1570) described its properties accurately; Libavius (1595) recognised the identity of the acids from different processes of preparation; the same was done by Angelus Sala (1613), who pointed out the fact, which had sunk into oblivion since Basilius, that sulphuric acid can be obtained by burning sulphur in moist vessels (of course with access of air); after that time it was prepared by the apothecaries in this way. An essential improvement, viz. the addition of a little saltpetre, was introduced in 1666 by Nicolas le Fèvre and Nicolas Lémery. This caused a sort of manufacture of vitriol which is said to have been introduced into England by Cornelius Drebbel; a quack doctor of the name of Ward first carried on sulphuric-acid making, on what was then a large scale, at Richmond, near London, probably a little before 1740. Ward employed large glass vessels up to 66 gallons capacity, which stood in two rows in a sand-bath, and which were provided with horizontally projecting necks; at the bottom they contained a little water. In each neck there was placed an earthenware pot, and on this a small red-hot iron dish, into which a mixture of one part saltpetre and eight parts of brimstone were put; then the neck of the bottle was closed with a wooden plug; on the combustion being finished, fresh air was allowed to enter the vessel, and the operation was repeated till the acid had become strong enough to pay for concentrating in glass retorts.

Ward called the product "oil of vitriol made by the bell" (already Basilius Valentinus had used the expression "per campanam" in this sense), in order to distinguish the spirit of vitriol made from brimstone from that distilled from sulphate of iron, the latter having been already before Ward's time made on a kind of manufacturing scale in England: an exact description of this is given by J. C. Bernhardt in his *Chemische Versuche und Erfahrungen*, 1755. Ward's process, troublesome as it is, reduced the price of the acid from 2s. 6d. per oz. (the price of the acid from copperas or from burning brimstone under a moist glass jar) to 2s. per lb.

An extremely important improvement in this process was the introduction of the *lead chambers*, which by general consent is ascribed to Dr Roebuck of Birmingham, who in 1746 erected such a chamber 6 ft. square, and in 1749, in partnership with Mr Garbett, built a factory, founded thereon, at Prestonpans in Scotland, in order to supply acid for the bleaching of linen. The mixture of brimstone and saltpetre in the proportion employed by Ward was put into small iron waggons which were run into the chamber on a railway: the chamber was closed, and the process carried on intermittently in this way. Guttmann (*J. Soc. Chem. Ind.*, 1901, p. 5) gives a detailed description and some drawings of such "lead-houses" and their style of working, from a manuscript by a Birmingham chemist, W. E. Sheffield, written between 1771 and 1790. The cost of acid of sp. gr. 1·844 per ton by that process was £22, 6s. 4d. without labour.

Soon other works followed at Bridgenorth, and at Dowles in Worcestershire, where the chambers were already made 10 ft. square; in 1772 a factory was erected in London with 71 cylindrical lead chambers, each 6 ft. in diameter and 6 ft. high. In 1797 there were already six or eight works in Glasgow alone. According to the statements given in Mactear's *Report of the Alkali and Bleaching-Powder Manufacture in the Glasgow District* (p. 8), the acid at that time cost the Glasgow manufacturers £32 per ton, and was sold at £54. At Radcliffe, near Manchester, it cost, in 1799, £21, 10s. per ton, without interest on capital. In the latter place there were 6 chambers 12 ft. long, 12 ft. wide, and 10 ft. high, with roofs like those of houses, and valves opened between each operation; on their bottom there was 8 or 9 in. of water; every four hours a mixture of 1 lb. saltpetre and 7 lb. brimstone was burned in each chamber on iron shelves, of which each chamber contained four, 4 in. distant one from another. The shelves were made of very thin iron, in order to get heated very quickly, and rested on iron frames, by means of which they could be slid in and out; a quarter of an hour before each operation the valves and doors were opened in order to allow air to enter. Thus weekly, 1386 lb. of brimstone and 198 lb. of saltpetre were burnt, yielding 1800 lb. of oil of vitriol—that is, 130 per cent of the sulphur, with a consumption of 14·28 per cent. saltpetre on the same. In six weeks the strength of the acid attained only 1·250 sp. gr.; it was then run off and concentrated up to 1·375 sp. gr., in which state it was used and sold. At Prestonpans, in 1800, a yield of only 111 per cent. on the sulphur was attained, with a consumption of 13 per cent. saltpetre on the brimstone; in 1813 there were in that place 108 chambers of 14 ft. length, 10 ft. height, and 4½ ft. width. In 1805 there existed at Burntisland a factory with 360 chambers of a capacity of 19 cb. ft. each.

R. Forbes Carpenter and W. F. Reid also give some interesting notes on the early manufacture of sulphuric acid (*J. Soc. Chem. Ind*, 1901, p. 7). The former mentions acid-chambers erected in Cornwall from dressed granite, with lead top and bottom.

In the meantime the first lead chamber in France had been erected at Rouen by Holker in 1766. In 1774, in that place, on the advice of De la Follie, an important improvement was introduced, viz. the introduction of steam into the chambers during the combustion of brimstone. In 1793 Clément and Desormes showed that the acid-chambers can be fed by a *continuous* current of air, by which a great deal of saltpetre could be saved. They showed that the oxidation of sulphurous acid takes place to the extent of nine-tenths at the expense of atmospheric oxygen, and that the saltpetre plays only the part of intermediary between the air and the sulphurous acid. By this demonstration the modern theory of the essence of the sulphuric-acid-making process was established; but it took a remarkably long time before the difficulties were overcome which stood in the way of introducing the continuous system into practice. Usually the introduction of the continuous burning of brimstone is ascribed to Jean Holker (a grandson of the first Holker), in 1810; but, according to Mactear, a continuous system had been introduced at St Rollox, at least partially, already in 1807; steam was first introduced there in 1813 or 1814.

In Germany the first lead chambers seem to have been those at Ringkuhl, near Cassel. One of the oldest chambers was that erected by Dr Richard at Potschappel near Dresden in 1820; as he had no plumber at his disposal, he had to solder the chamber himself with soft solder and a smoothing-iron (Bode, in his translation of H. A. Smith's *Sulphuric Acid Manufacture*, p. 96). This chamber was still charged intermittently, 100 lb. of brimstone yielding only 150 lb. of vitriol.

Lampadius, in a treatise published in 1815,[1] speaking of sulphuric acid as then made in England and at Schwemsal, near Leipzig, describes the lead chambers as "rooms," about 25 ft.

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[1] Quoted by Cl. Winkler, *Z. angew. Chem.*, 1900, p. 731. Some of the following statements are also taken from this paper.

square with a stone floor, lined throughout with lead, with two doors through which sulphur is introduced and burned on iron dishes, holding ½ cwt. of brimstone, mixed with 20 per cent. nitrate of potash, steam being introduced from a copper outside the room. Through four pipes and taps, during the later stages of the combustion (which lasted three hours), a little air was admitted. The "room" was exposed to great strain through the strong expansion and subsequent contraction of the atmosphere inside. The dilute acid formed was boiled down in glass retorts to sp. gr. 1·800.

The invention of soldering lead, not with "soft solder," but with lead itself, generally called "burning," by means of the hydrogen blowpipe, is due to Debassayns de Richemond, in 1838. As late as 1846 Prechtl's *Technical Encyclopædia* (xiv. p. 246) mentions the chamber-sides as being sometimes covered with a crust of chamber-crystals, ½ or 1 inch thick, which proves the want of understanding the process at that time.

Kestner, of Thann in Alsace, was the first to collect the products of condensation at the chamber-sides in order to regulate the working of the chambers thereby. This innovation was at once considered of such importance that Kestner was called to Glasgow in order to introduce his plan into Tennant's works.

In 1827 Gay-Lussac's condensing-apparatus for the nitre-gas escaping from the chambers was invented: at Chauny this apparatus was erected in 1842, at Glasgow in 1844. But we have now come so near the present time that we may conclude the historical part of our task.

An interesting account of the development of the industry of "oleum" and of ordinary sulphuric acid in Austria is given by Martell in *Chem. Ind.*, 1911, pp. 205 *et seq.*

General Principles of the Manufacture of Sulphuric Acid.

Sulphuric acid can be obtained on a large scale in one of two ways—viz., either by burning sulphur or sulphides into sulphur dioxide and further oxidising the latter, or by decomposing natural or artificially prepared sulphates. The latter process, apart from several proposals so far not carried out practically, has for a long time past served for making fuming oil of vitriol, which will be treated of in a special chapter;

ordinary sulphuric acid has always been obtained by the former process, which will occupy us in the first instance.

By the *combustion of sulphur*, either free (as brimstone, gas-sulphur, etc.) or combined with metals or with hydrogen, *sulphur dioxide* (SO_2) is always formed at first. Sulphuretted hydrogen, even when mixed with as much as 70 per cent. of inert gases (nitrogen), can be lighted like illuminating-gas and continues burning without any difficulty, aqueous vapour being formed at the same time as SO_2. Brimstone ignites in the air at a temperature rather below 300° C.; and when once it has begun to burn, the heat generated raises the whole of the sulphur to the point of ignition, provided that sufficient air be present. A number of metallic sulphides behave similarly: the most important of these for our purpose is the iron disulphide, FeS_2; but here special precautions must be taken, so that the whole mass may be completely burned (roasted). In both cases, besides sulphur dioxide, SO_2, a little trioxide (sulphuric anhydride), SO_3, is always formed, and, in the presence of water or steam, also sulphuric acid, SO_4H_2, more or less diluted with water. Moreover, an aqueous solution of sulphurous acid in contact with air gradually changes into sulphuric acid. In both cases it is, of course, the oxygen of the air which converts the SO_2 into SO_3 or SO_4H_2; but this reaction at the ordinary or only moderately elevated temperature goes on far too slowly to be applicable for technical purposes.

There are two ways of increasing the velocity of the oxidation of sulphur dioxide. One of these, which is principally applicable to dry gases and therefore leads to the preparation of sulphur trioxide in the anhydrous state, is the employment of *catalytic* or *contact* substances. We shall discuss this in a special chapter.

The second way, which is exclusively applicable to the production of real sulphuric acid, H_2SO_4, is founded on the property of the acids of nitrogen to serve as carriers of oxygen from atmospheric air upon sulphur dioxide and water, the original nitrogen oxide being always reformed. This process will be explained in detail when we treat of the theory of the formation of sulphuric acid; it is called the *lead-chamber* or *vitriol-chamber process*.

The reaction between nitrogen acids and sulphur dioxide goes on only in the presence of water; and we must add at once that, in practice, much more water is needed than suffices for the formation of SO_4H_2; the sulphuric acid formed is therefore always *dilute*, and must be *concentrated* for most purposes.

For some purposes the acid must also be deprived of certain foreign substances which get into it from the raw materials and the apparatus; and in such cases the sulphuric acid has to be purified.